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INSTRUMENTAL ANALYSES FOR WET SCRUBBING PROCESSES

E. A. Burns, et al

TRW Systems Group

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INSTRUMENTAL ANALYSES FOR WET SCRUBBING PROCESSES

CONTRACT 68-02-0007

by

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INTERIM REPORT

Prepared for
ENVIRONMENTAL PROTECTION AGENCY
Office of Air Programs
Research Triangle Park
North Carolina

15 JANUARY 1972

TRW
SYSTEMS GROUP
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FOREWORD

This document constitutes the interim report for the work accomplished between 16 November 1970 to 31 December 1971 by TRW Systems for the Environmental Protection Agency, Office of Air Programs, Durham, North Carolina, under Contract 68-07-0007 on Instrumental Analysis for Wet Scrubbing Processes. This work was conducted under the direction of Dr. Robert M. Statnick of the Office of Air Program, Durham, North Carolina.

The Applied Chemistry Department and Chemical Engineering Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division, were responsible for the work performed under this program. Mr. B. Dubrow, Manager, Chemistry and Chemical Engineering Laboratory provided the overall program supervision and Dr. E. A. Burns, Manager of the Applied Chemistry Department was Program Manager. The Principal Investigator was Mr. A. Grant. Major technical contributions throughout the program were provided by Messrs., D. F. Carroll, M. P. Gardner and J. C. Gray. Acknowledgment is made of technical assistance provided during the program by the following TRW Systems personnel:

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ABSTRACT

The development of control methodology for sulfur oxide and particulates from power plant emissions by wet scrubbing processes requires accurate and reliable measurements of process variables. Planned EPA process demonstration studies will result in a requirement for a large number of chemical analyses requiring 1) automatic instrumental methods and 2) associated data acquisition and processing capabilities which exceed current instrumental capabilities. This report describes activities undertaken at TRW Systems under Contract 68-02-0007 toward the development of methods suitable for optimization and control of the wet limestone and dolomite scrubbing processes by continuous onstream analytical methods. Emphasis was placed on development of continuous on-line methods for slurry sampling and separation that do not disturb the chemical steady state condition. Establishment of sampling requirements and an effective means for total phase separation in a period less than thirty seconds were accomplished.

Analytical instrumental methods having capability of continuous or slug flow analysis within two minutes were identified for characterization of the separated solid matter and liquor. Analytical methods were identified which permit continuous X-ray analyses of solid constituents for sulfur, calcium, magnesium and iron contents. Liquid phase analyses methods were established for instrumental analysis of acidity, sulfite, sulfate, calcium, magnesium and carbonate contents. A new method for rapid analysis of sulfite were developed. content based on furfural bleaching is being carried to a state of prototype analytical instrument development. In addition, approaches for total complete on-line analysis of other wet limestone scrubber constituents have been identified. (M)

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INSTRUMENTAL ANALYSES FOR WET SCRUBBING PROCESSES

by

E. A. Burns, A. Grant, D. F. Carroll, M. P. Gardner and J. C. Gray

SUMMARY

This interim document presents the work accomplished by TRW Systems during the period 16 November 1970 to 31 December 1971 for the Environmental Protection Agency, Office of Air Programs, under Contract 68-02-0007. The objective of this program was to identify instrumental analysis methodology suitable for laboratory and especially on-line analysis of selected species in and properties of wet scrubber process streams from pollutant emission control systems. The emphasis during this program has been placed on the development of on-line sampling and separation techniques to provide separation of the slurry system into solid and optically clear liquid phases and analysis and measurement methodology for pH, sulfite, sulfate, calcium, magnesium, carbonate, nitrite and nitrate. This phase of the program was organized in three tasks in order to accomplish the stated objectives:

- TASK I - Development of Laboratory Instruments and Analysis
- TASK II - Development of Process Instrumentation
- TASK III - Data Acquisition and Processing

Upon review of analysis requirements and process characteristics, effective sampling, separation and quenching of reactants was identified as a major prerequisite to development of analysis methodology. Several centrifugation and filtration techniques were evaluated in terms of rapid phase separation at the point of process sampling for a sampling criterion of 30 grab samples per hour minimum. The system designed and developed in the laboratory utilizing actual and simulated slurries (3% nominal loading) and recommended for field evaluation is comprised of a one gpm cyclone (cone) stage followed by a dual-parallel filter stage for polishing the liquid stream. This system may also permit continuous operation, if necessary, as the dual in-line filters are of high capacity-quick interchange design.

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One instrumental analysis technique, namely, x-ray fluorescence (XRF) was shown to provide on-stream or laboratory elemental analysis capability for unseparated slurry as well as separated liquid and solid phases. The unit recommended for the on-stream application is an ARL Model PCXQ which can accommodate up to 15 slurry streams and with nine spectrometers to determine nine elements from magnesium and heavier. Sensitivity for total sulfur, especially important in the analysis of slurry was found to be 0.03% for solid samples and considerably better than 0.25% for the mixed slurry. For solids analysis, XRF was shown to be the optimum method for calcium, magnesium, iron, silicon and other metals of concern, offering a significant saving in time and cost per analysis compared to other candidate techniques.

Atomic absorption spectrometry (AA) was evaluated in the laboratory for determination of those species very slightly soluble or present in trace quantities in the liquid or solid phase (after dissolution). AA is recommended specifically for dissolved calcium, magnesium, iron, potassium, sodium and other trace elements. This method is especially valuable where secondary pollution problems from mercury, arsenic, chromium, lead, etc., must be monitored and controlled.

During the review of candidate analytical methods for the continuous determination of dissolved sulfur dioxide (HSO_3^- and $SO_3^=$) it was determined that no satisfactory methods existed for determining concentrations in the range to be found in the limestone slurry mixture. A new method based on bisulfite bleaching of the furfural UV absorption was developed to facilitate this analysis. This method is based on the chemical bleaching of the 276 *nM* absorption of furfural by reaction with bisulfite. Detailed studies of the effect of pH, diverse ions, temperature and time to constant color development has resulted in the selection of a single reagent addition consisting of furfural, phosphate buffer and sulfamic acid (to eliminate interference from trace concentrations of nitrite). The reproducibility of the method has been determined to be better than 2% relative or 0.2 *mM* absolute whichever is higher. A preliminary design of a prototype plug flow automated analyzer to accomodate up to ∿100 samples per eight-hour shift has been completed.

Methods for the analysis of sulfate, carbonate, nitrite and nitrate were evaluated theoretically and experimentally less extensively than those above utilizing simulated slurry liquid samples. Two state of the art methods for sulfate determination were found to warrant further consideration and development, i.e., sulfate precipitation by barium with the measurement being accomplished by turbidimetry or by AA, and 2) ion exchange with barium chloranilate and colorimetric measurement of free chloroanilic acid. Feasibility tests demonstrated the potential utility of a pyrolysis/acidimetric carbonate determination. Released CO_2 could be measured readily by NDIR in a batch automated or continous analyzer. In this phase of the program nitrite/nitrate literature was reviewed and several were selected for further consideration and future experimental evaluation.

A basic modular designed bench scale test loop wet scrubber unit was fabricated to permit evaluation of the recommended methods under simulated use conditions. A loop system was selected because of the necessity of: 1) closely approximating the full scale operating unit, 2) accurate control, and 3) producing stable (equilibrium) and unstable (non-equilibrium) conditions for evaluating candidate instruments under known, controllable conditions with realistic compositions. The system consists of a bench scale Venturi scrubber with a second stage packed bed, fitted with a recirculating gas stream and slurry pumping capability to approximate actual L/G ratios to be tested on pilot and full scale scrubbers. Equipped with ports for acquiring appropriate gas and slurry samples and a continuous pH monitor in the scrubber downcomer, the scrubber experiments 1) demonstrated the adequacy of the proposed methodology, and 2) contributed significantly to the elucidation of the chemistry of the scrubbing process. Process variables that were studied and found to impact process chemistry were oxygen content, fly ash loading and composition, and temperature. Sulfite oxidation and rate of sulfite precipitation were two such important effects that were isolated in these studies.

Recommendations were provided for data acquisition and process equipment suitable for use with recommended analytical instrumentation and capability for interfacing with the engineering computational system to be operational at the TVA wet scrubber plant site. The primary candidate system was the Hewlitt Packard 2411C computer because of its proven application with the recommended ARL PCXQ 4400 X-ray fluorescence unit. An alternative computer data process for the analytical instrumentation was the Digital Equipment Corporation PDP 12/LDP.

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1.0 INTRODUCTION

This interim report presents the work accomplished by TRW Systems for the Environmental Protection Agency, Office of Air Programs, under Contract 68-02-0007 during the period 16 November 1970 to 31 December 1971. This program consisted of analytical and experimental studies aimed toward the identification of instrumental methods suitable for on-line analysis of selected chemical species in the Shawnee Plant limestone wet scrubbing processes. The underlying motivation for conducting this program was to develop methods suitable for continuous monitoring of the key chemical species to facilitate 1) an understanding of the wet limestone scrubbing process, and 2) provide mass balance information related to the effectiveness of the process for the abatement of sulfur dioxide emissions from stationary power sources.

The development of control methodology for sulfur oxide and particulates from power plant emissions by limestone/dolomite wet scrubbing requires accurate and reliable measurements of process variables. Efficient, proven methods for many of these measurements have not yet been developed. The monitoring of the complex chemistry involved in this scrubbing process and associated sampling of representative samples in quiescent and dynamic mixtures of liquors, slurry and solids are in themselves challenging analytical problems. In addition, planned OAP process demonstration studies at the Shawnee Power Plant, Paducah, Kentucky, will result in a requirement for a large number of chemical analyses requiring 1) automatic instrumental methods and 2) associated data acquisition and processing capabilities which exceed current instrumental capabilities.

The chemistry of the process is not sufficiently understood at the present time because of the lack of definitive mass balance information involving the chemical species existing in the scrubbing solution. The development of suitable on-stream analysis methods will provide a means to fill this gap through detailed characterization of the process. High analytical accuracy (e.g., 0.1% relative) is not a requisite of the needed methods but rather they must be adaptable to instrumental techniques that will be reliable, reproducible, cost effective and employ hardware requiring little maintenance.

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The objective of the program reported here was to carry out systematic analytical and experimental studies for development of laboratory instrument and analysis methods, development of process instrumentation and outline data acquisition and processing requirements suitable to handle the on-line information to be generated in the process demonstration studies.

Task I of this program consisted of identification and/or development of analysis methods for critical chemical species in the liquids, slurry and solid materials resulting from the aqueous limestone scrubbing of fossil fuel combustion gases. The intent of this effort was to identify instrumental methods based on their specificity, reproducibility, potential lag time, and reliability of operation. Specifically, the task involved a review of available literature information on the primary candidate wet scrubbing process (limestone), identification of applicable analysis methodology and instrumentation, preparation of generalized instrument specifications and experimental evaluation of the methods developed using laboratory samples.

The Task II efforts consisted of the evaluation of the applicability of the methods identified in Task I to continuous on-line instrumentation for monitoring selected species in the liquid, slurry and/or solid phase at several locations in the scrubber system. As part of this evaluation, the methods were tested in a laboratory bench scale simulated process which involved both stable and unstable slurry systems. Again, the reliability, sensitivity, reproducibility, specificity and accuracy of the measurements were used as criteria for evaluating candidate instruments, breadboard prototypes and modified apparati.

Task III efforts consisted of identification of applicable data handling systems for collecting and reducing all information produced by the analysis scheme in a form which lends itself to computer input. From the studies conducted during this program, recommendations for future needed research and development activities in the area of characterizing process streams for mass balance purposes have been generated.

This report is divided into three principle sections covering the program tasks: 1) development of laboratory instruments and analysis, 2) development of process instrumentation and 3) data acquisition and processing.

The significant conclusions reached from evaluation and assessment of the results are listed together with recommendations for activities that warrant further investigation. This report identifies in a special section the new technology originating from the program. The information presented in the main body of this report is supplemented by appendices covering detailed descriptions of procedures, assessment of candidate analytical procedures, and lists of vendors and manufacturers which offer suitable equipment.

2.0 TASK I - DEVELOPMENT OF LABORATORY INSTRUMENTS AND ANALYSES

This task was aimed at identification and/or development of analysis methods for critical chemical species in the liquids, slurry and solid materials resulting from the aqueous scrubbing of fossil fuel combustion gases. In accordance with EPA direction, TRW concentrated its activities on the measurement of the following chemical species and characteristics of the wet scrubbing process:

- Calcium concentration
- Magnesium concentration
- Sulfite concentration
- Sulfate concentration
- pH
- Ionic strength

During the conduct of this effort it was determined that many of the analytical methods suitable for laboratory characterization of the limestone scrubber constituents were not applicable to the planned future on-line characterization. On the other hand, most of the analytical methods suitable for on-line use are also acceptable as laboratory methods. This observation, together with the subsequent initiation of a parallel program to the Radian Corporation, (Reference 1) for development of a laboratory analysis scheme resulted in the relative de-emphasis of Task I activities relative to those of the on-line instrumental analytical methods. An assessment of the early plans by Bechtel Corporation for sampling points and analysis requirements indicated that after an initial evaluation period, on-line process control measurements were required to be cost effective.

However, the comprehensive literature survey for laboratory experimentation conducted in Task I provided the basis for 1) identification of analysis and characterization criteria, 2) establishment of on-line or automated process instrumentation specifications, and 3) development of acceptable methodology. The following section describes the

1. Literature review of available information on the primary candidate wet scrubbing process,
2. Analysis methodology and instrumentation,

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3. Generalized instrumentation specifications, and
4. The methods developed and evaluation pertaining to laboratory analysis.

2.1 LITERATURE REVIEW

The literature review was initiated in order to update and maintain currency of our compilation of data on instrumental and automated manual analytical methodology for wet scrubbing processes. The literature review was aimed at obtaining data on:

- Solubility of slurry constituents
- Methods of analyses outlined in laboratory studies, and
- Applicability of current instrumentation to the laboratory study

2.1.1 Theoretical Modeling of the Wet Scrubbing Process

Key related reports generated under EPA sponsorship have been reviewed to provide background information. Throughout the review there appeared to be a lack of applicable information concerning the chemical species which exist under the actual temperature and chemical conditions of the wet scrubbing process. Because of the lack of empirical data, EPA has sponsored several efforts aimed at providing a theoretical description of the process suitable for identification of future process design improvement. The leading process model is that generated by the Radian Corporation (Reference 2) which describes the process through chemical compositional computation using equilibrium conditions. This model has proven to be very useful as a starting point in identifying the chemical composition of the wet limestone slurry at various points in the process under fixed conditions. It is generally recognized that there are shortcomings to the equilibrium assumption, however, modification of the model to provide a "real-life" process model have not been undertaken primarily because of the lack of empirical information needed for confirmation.

As part of this task, TRW reviewed the Radian model in detail to determine its applicability to describe the scrubber chemistry. It is the intention of this review to identify some of its limitations and point out how it can be further improved. These shortcomings are delineated below:

- The most significant shortcoming is the assumption of equilibrium conditions. Recent experiments at TRW (see Section 3.5.3) have clearly identified that the solids do not precipitate to their equilibrium value in a time period to be consistent with either the scrubber or effluent hold tank.

- Several of the chemical species used in the theory have not been substantiated and are inferred by calculations aimed at making an internally consistent set of data (without cross check).

- The constants used in many cases were determined by experimental techniques which are open to technical question [use of specific ion electrodes which tend to have errors in response, particularly at moderate (10^{-3} *M*) concentrations].

- The model requires the input of many variables which might be determined theoretically. These include the quantity of NO_x dissolved (which has been shown to be considerably lower than that used in the calculations), the amount of CaO and MgO converted to hydrate and the amount of SO_2 oxidized to SO_3.

- Several chemical species which are known to exist in partially oxidized sulfite solutions, namely, the thionates, $S_2O_6^=$ and $S_3O_6^=$ have not been considered in the theoretical treatment.

- The thermochemical equilibria in solutions are quite sensitive to properties, such as ionic strength, but most of the data utilized in the formulation of the model were taken from pure compound solubilities and assuming the validity of the extended Debye-Huckel Law.

- Another assertion which has a strong bearing on the chemical composition is that use of Fuoss equation is valid for determining the temperature dependence of the constants.

Lacking more definitive information during the early phases of the program, analysis error requirements for the key chemical constituents present in the limestone/dolomite scrubber were based on estimates provided by the EPA Project Monitor of concentration range and relative error of the methods required for 20% sulfur mass balance closure as determined by the Bechtel Corporation. These data are presented in Table I and were used to guide the direction of the program pending updating of these requirements in concurrent programs by the Radian Corporation and Bechtel Corporation.

TABLE I

LIQUID ANALYSIS REQUIREMENTS

	Concentration Range, *mM*	Maximum Allowable Relative Error*
Mg^{++}	1 - 1000	3
Ca^{++}	1 - 250	3
$SO_3^{=}$	1 - 150	3
$SO_4^{=}$	1 - 500	5
$CO_3^{=}$	1 - 20	15
Na^{+}	1 - 500	15
K^{+}	1 - 500	15
Cl^{-}	1 - 500	15

*For 20% sulfur mass balance closure

2.1.2 Review of Analysis Methodology and Instrumentation

Available literature on analytical procedures used to characterize the major chemical constituents in limestone slurries were reviewed. Table II provides a summary of the methods that have been recommended and information concerning the technique and its applicability to slurry solid, liquor or mixed phases together with appropriate comments relating to end point and/or alternative detection procedures. In general, the prior investigations were conducted over a short period of time and little, or no information was provided concerning the utility of the methods for continuous on-line measurement. The methods were used without consideration of potential interferences and their effect on the accuracy and reproducibility of the methods.

Concurrently, analytical techniques were compiled for characterization of cations and anions that were expected to be present in the slurry liquor. Appendix A delineates the wet and some standard instrumental methods for sixteen of the key chemical species. Tabulated are the components to be measured, the principle of method, sensitivity, interferences and related comments. In general, utilization of these methods requires separation of phases prior to analysis.

TABLE II

LITERATURE RECOMMENDED ANALYTICAL PROCEDURES FOR MAJOR SPECIES IN LIMESTONE SLURRIES

Component	Referee	Rapid	Phase*	Comment	Alternate	References
Ca, Mg, Na, K, Fe, other metals	AA	AA	(S & L)	-	Na+K flame photometric; EDTA for Ca and for hardness. Glyoxal 2-hydroxyanil (color)	3
Total Ca and Mg	Titrimetric (EDTA)	-	(L)	-		2
NO_2^-, NO_3^-	Photometric	Photometric	(L)	-	NO_3^- Brucine; NO_3^- Phenoldisulfonic acid. NO_3^- polarographic; NO_2^- diazotization	3
NO_3^-	Gravimetric	-	(L)	Weigh as $C_{12} H_{22} TlNO_3$		2
$SO_3^=$	Titrimetric	Titrimetric	(L & S)	I_2-phenyl-arsine oxide (amperometric)	HBr-electrolytic titration**	3
$SO_4^=$	Gravimetric	Colorimetric		Turbidimetric	Barium chloroanilate-colorimetric titn. $Ba(ClO_4)_2$-thorin	3 3
Cl^-	Titrimetric	Titrimetric	(L)	$AgNO_3$-potentiometric	Mercuric nitrate	3
$CO_3^=$	Titrimetric	-	(L & S)	$Ba(OH)_2$-titn with HCl		3
Total $CO_3^=$	Manometric	-	(S)			2
Trace Metals	Emission spec.	AA	(S)	-	Polarography	3
pH	Glass electrode	Glass electrode	(TS)	-		3
Conductivity	-	Probe	(TS)	-		3
Suspended solids	Gravimetric	Radiometer	(TS)	-	(Ca, Mg, Na, K, Cl^-, NO_2^-, NO_3^-, SO_4 and trace metals ion-selective electrodes)	3

*S = solids; L = Liquids; TS = total slurry

** Considered by EPA

Of the standard manual laboratory methods for sulfite and sulfate, the iodometric redox methods are still generally preferred for the lower oxidation states, while for sulfate ion the most widely accepted methods are based on the barium titrations with a visual end points and barium precipitation with a gravimetric determination (carbonate and sulfite interfers and must be removed). The strontium-EDTA method (see Appendix A, Reference 4) for differentiating carbonate and bicarbonate, which appears to offer a distinct advantage over other methods, remains to be evaluated. Cation analysis is commonly performed by the complexometric EDTA and colorimetric methods, however, atomic absorption spectrophotometry and specific ion electrode methods provide distinct advantages over the classical methods in simplicity, specificity and economy.

Electrochemical methods appear to be the prime approach for determination of dissolved oxygen in process streams which is considered to be highly significant in the liquid phase oxidation of sulfite and bisulfite. Additionally, the sulfite ion concentration in the liquid phase of the wet scrubber process stream may be suited to electroanalytic measurements [e.g., in the millimolar (*mM*) concentration range]; the actual dissolved oxygen content in these solutions is somewhat in question, however, dissolved oxygen from air (in non-reactive media) at wet scrubber process stream temperatures is $\sim$0.5 *mM*. The process stream at a pH of near 6 will possess major components of HCO_3^-, $SO_4^=$, HSO_3^-, H_2CO_3, Na^+, Mg^{+2}, Ca^{+2} and $CaSO_4$. These major cations do not interfere with the electrochemical process and any other reducible metals originating from the fly ash will be at a concentration of at least two orders of magnitude less, hence, will be insignificant relative to the sulfite and dissolved oxygen content. One requirement the electrochemical method has is that the liquid should be free of fine suspensions.

A critical review of current methods used for analysis of dissolved oxygen and dissolved sulfur dioxide by polarographic, chronopotentiometric, conductometric, coulometric and other methods were reviewed. Criteria used for evaluation of the various methods included:

- The present state of development (laboratory technique, availability of laboratory or process stream instruments)
- Sampling mode
- Specificity and interferences
- Pretreatment of sample for analysis (concentration, filtration, adjustment of pH)
- Useful concentration range, sensitivity, accuracy, precision
- Temperature requirements
- Analysis time
- Data reduction capability
- Requirements for further development
- Maintenance requirements
- Cost
- Life time and cycle life
- Commercial instruments

The detailed compilation of this information is in tabular form in Appendix B for possible future implementation of an experimental investigation.

Numberous candidate state of the art instrumental techniques for wet scrubber constituents were evaluated experimentally as well as theoretically, including some of the standard photometric (colorimetry, turbidimetry, atomic absorption, etc.) techniques listed in Appendix A. The following specific techniques are discussed in detail in subsequent sections of this report.

Electrochemical Methods
Atomic Absorption (AA)
X-ray Fluorescence (XRF)
UV-VIS-NIR and IR Spectrophotometry
Electron Diffraction
Colorimetry
X-ray Diffraction (XRD)
Flame Emission

Quantitative automated laboratory or instrumental techniques were successfully developed and demonstrated for:

- Cations and elements by AA (in solution) and XRF (solids and liquids), and
- Sulfite by a new UV spectrophotometric method.

The feasibility of laboratory automatable methods for the following species was also demonstrated:

- Sulfate by turbidimetry
- Sulfate by high frequency titrimetry
- Carbonate by CO_2 liberation and NDIR detection

2.2 GENERALIZED INSTRUMENTATION AND SLURRY SAMPLER SPECIFICATIONS

As a result of the review of the sampling and characterization requirements of the limestone dolomite wet scrubbing SO_2 abatement process through both review of literature and visits to operating facilities, generalized specifications for instruments to monitor the wet scrubbing process and sampler systems have been generated. These general specifications are presented below for use as guidelines in purchasing various types of instruments which will be required. Specific types of instrumentation are recommended later in this document.

2.2.1 General Instrument Specifications

- Selectivity - Measure $SO_4^{=}$, HSO_3^{-}, H^{+}, Ca^{++}, Mg^{++} and the other identified species of concern and be relatable to the content of the original wet scrubber stream at the time of sampling.
- Calibration - Capable of calibration and standardization by a chemical and/or instrument technician or a person of equivalent training and experience.
- Routine Operation - Capable of attended operation with no more than four simple calibrations per day as accuracy checks.
- Maintenance/Repair - Capable of being maintained by a qualified chemist or chemical technician with a maximum of two days special training. Capable of repair by a chemical instrumentation technician who has received reasonable maintenance and repair training.

- Operating Voltage and Voltage Variations - Capable of operation at 120 or 240 volts A.C. with line voltage variations which may exceed ±30%.
- Accuracy and Reproducibility - It is desired (but not always possible) that all instruments will be relatable after calibration to ±5% of the true value for the species being measured.
- Output Signals - All output signals where practical should be 100 mv or compatible with a specific readout system if so specified.

2.2.2 Operating Specification

The operating specifications for each instrument will depend on principles of measurement, sampling methods and end use requirements. Specifications defined at this time include:

- Ambient Conditions - Instruments must be capable of operation in the presence of or protected from the coal dust, dirt, temperature extremes, vibrations, etc., encountered in and around an enclosed coal burning power station.
- Sampling Time - A sample rate of 30 samples per hour per species being measured is desirable.
- Response Time - Direct instream analysis is desirable, however, when not practical a time delay between sample collection and data presentation is acceptable if such data is directly relatable to the process sample point at the time of sampling. A maximum analysis time of two minutes per sample per species is desirable.

2.2.3 Requirements for Slurry Sampling and Separation

In order to achieve separation between the solids and liquids of a non-equilibrium slurry a rapid separation is required to "freeze" the components of the non-equilibrium system.

- Slurry Sample Rate - In order to minimize perturbation of the scrubber system not more than 1% of the stream v/v should be sampled.

System Flow Rate	Max. Sample Flow Rate
150 gal/min	1.5 gal/min
600 gal/min	6.0 gal/min
1200 gal/min	12.0 gal/min

- In-Stream Sampling Velocity - Because of the nature of wet limestone slurries and the broad distribution of particulate sizes, conditions approaching isokinetic sampling are desirable. The sample flow velocity at input point should be held within two times that of the actual stream velocity at that point. This deviation will depend on particle size, particle distribution, turbulence, etc.

- Sample Probes - Removal probes should be of such design and construction so as to remove a representative sample.

- Lag Time - From time of sampling, complete separation to pure liquid and solid phases should not take more than ~30 seconds. It can be assumed that if "all other things are held constant" the resulting samples will be representative for elements at least in the system at an equal flow time down stream of the sample time.

- Materials of Construction - In all cases care must be exercised to ensure that all surfaces subject to sample contact be an inert non-reactive material.

- Sample Transfer Lines - All sample transfer lines should be constructed of inert material, e.g., Teflon, maintained at the sampling point temperature and as short as practical to minimize dead volume.

- Particulate Size Solids Sample - The separation device must be capable of providing an optically clear liquor from a slurry containing particles ranging from less than 0.5 micron to over several hundred microns.

- Solids Content - The solids separation system must be able to handle solids loadings ranging from less than 3% to over 15% (w/w).

- Drying of Solids - A non-reactive solvent should be utilized to wash the solids before final drying in order to remove the liquid phase components present.

- Maintainability, Cleaning - The solids sampling system must be easily cleaned. Backflush components or throwaway cartridge filters are recommended.

- Power Requirements - Pumps and other electrical devices should operate at 120 V AC ±30V.

2.3 REVIEW OF LIMESTONE WET SCRUBBING PROCESS OPERATION

As an integral part of the survey of the state of the art for limestone wet scrubbing processes and for the purpose of identifying realistic process characterization needs, several meetings were held with process development engineering firms. Technical interchange (T.I.) meetings were held with key engineering and chemistry personnel at Bechtel Corporation, at their San Francisco facility, Zurn Environmental Engineers at their pilot scrubbing installation at Key West Electric Company, and Kansas Power and Light (KPL) to review the Combustion Engineering Company process. Field samples of scrubber slurry were obtained and phase separation techniques evaluated at the latter facilities. At a T.I. meeting held at TRW with EPA and TVA personnel, tentative recommendations of separation and analysis methods were discussed and numerous TVA synthesized samples of slurry components were transmitted for the purpose of methods evaluation. The following paragraphs present the highlights of the process reviews and the sampling that was accomplished. The resultant experimental effort are described under the appropriate methodology headings.

2.3.1 Review of the Shawnee Process Demonstration Operation

The operation procedures planned by Bechtel Corporation for implementation at the Shawnee Power Plant wet scrubbing process demonstration were reviewed. In addition to detailed discussion of the three types of scrubber designs, namely, Venturi, TCA plastic ball and flooded marble bed designs, information was provided concerning both process and instrument diagrams and the planned operational modes for investigation of several different configurations. After examination of the planned sample port locations, it was concluded that sufficient sample ports will be available in the planned facility. Because Bechtel had a cut-off time of January 28, 1971 for freezing the design of the plant hardware, any future recommendations were not compatible with this time frame. If it should be necessary to add new sample ports, this can be implemented by modifications of flanged sections of the process stream piping hardware. A complete package of Bechtel's planned operational mode sheets is given in Appendix C.

2.3.2 Inspection of the Zurn Engineering Wet Limestone Scrubbing Operation at the Key West Electric Company

As indicated above, the field trip to operational wet scrubbing facilities had the express purpose of determining methodology and equipment currently employed for process characterization, to evaluate sampling schemes and to acquire real samples for methods evaluation and development. With the cooperation of Zurn Environmental Engineering the pilot limestone and coral wet scrubbing process unit operated at the Key West Electric Company was inspected and sampled by A. Grant and E. A. Burns on January 13, 1971. This unit was scrubbing 1/8 of the flue gas from a 20 megawatt boiler burning a fuel oil containing 0.6% sulfur. The scrubber apparatus consisted of a modified particulate removal unit which provided turbulent mixing and a high level of liquid/gas contact. The inlet gas had a temperature of 250°F and a flow rate of 935 SCFM. The scrubbing solution studied during the run inspected by TRW representatives consisted of a 3% w/v limestone slurry. Table III lists the temperature and pH of the scrubbing unit slurry at various locations in the system. Instrumentation used by Zurn consisted strictly of monitoring the sulfur dioxide conent in and out with a Whittaker Dynascience instrument. To assist in defining problems associated with phase separation and species isolation, some exploratory experiments were conducted with the assistance of Dr. John Craig of Zurn Environmental Engineering.

TABLE III

CHARACTERISTICS OF ZURN LIMESTONE SLURRY

Location	Temperature (°F)	pH[a]
Inlet	78	7.76
Hopper	135	6.18
Weir Bottom	125	6.18
Spent Slurry	124	6.14
Filter Slurry		6.05

[a] Obtained using a Welch Sargent pH Meter equipped with automatic temperature compensation

The apparatus shown schematically in Figure 1 was used to provide filtration separation of one liter within one minute. This apparatus 1) consists of valving, manifold, filter and sample bottle, and 2) provides a uniform, representative flow through the manifold in the by-pass mode of operation. In the by-pass mode the remainder of the manifold was purged with gaseous nitrogen (to eliminate residual air which could possibly oxidize sulfite species in the slurry during subsequent handling operations). Activation of the by-pass valve and vacuum pump initiated flow of slurry from the bottom of the scrubber weir through the in-line filter unit (3 micron nominal size). The filtered liquid was optically clear and showed no evidence of particulate matter. In separate experiments the separated solids were 1) flushed with an inert halocarbon liquid (trichloroethylene) or alternatively, 2) flushed with dry nitrogen to quench any possible post sampling reactions of the solids.

Post sampling treatment of the liquids to inhibit subsequent reaction of sulfite to sulfate was accomplished as shown in Table IV. In addition to obtaining liquid and solid samples from the scrubber unit, samples were also obtained at both the make up water and starting limestone, as well as 55 gallons of spent scrubber slurry which was used in the evaluation and development of candidate separation techniques.

TABLE IV
SULFITE FIXATION EXPERIMENTS ON FILTERED WEIR BOTTOM
LIMESTONE SLURRY LIQUOR

Treatment	Purpose	Resulting pH	Observations
1:10 v/v 8-hydroxy quinoline solution (∿10%)	To complex metals and inhibit catalytic reactions.	6.05	Copious yellow precipitate
1:10 v/v glycerin	To retard sulfite oxidation	6.22	Clear liquid
1:10 v/v glycerin plus 1:5 v/v formaldehyde solution (37% w/w)	To retard sulfite oxidation and form stable aldehyde-bisulfite complex	9.11	Clear liquid

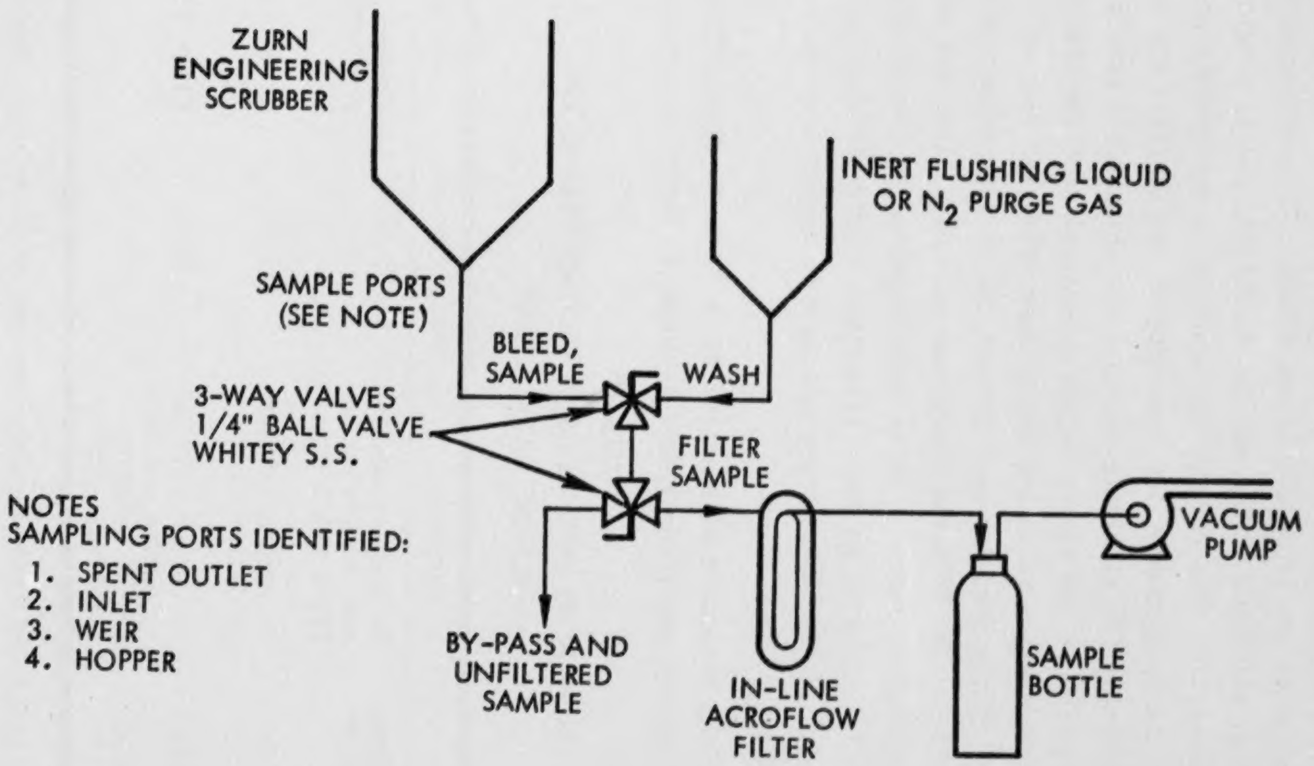

ZURN ENGINEERING SCRUBBER
INERT FLUSHING LIQUID OR N_2 PURGE GAS
SAMPLE PORTS (SEE NOTE)
BLEED, SAMPLE
WASH
3-WAY VALVES 1/4" BALL VALVE WHITEY S.S.
FILTER SAMPLE
NOTES
SAMPLING PORTS IDENTIFIED:
1. SPENT OUTLET
2. INLET
3. WEIR
4. HOPPER
VACUUM PUMP
BY-PASS AND UNFILTERED SAMPLE
IN-LINE ACROFLOW FILTER
SAMPLE BOTTLE

Figure 1. Sampling System for Zurn Wet Scrubber

These studies demonstrated that rapid filter separation of the slurry can be accomplished under anaerobic conditions in short periods of time and laid the foundation for the recommended sampling/filtration procedure for continuous sampling (See Section 3.1).

2.3.3 Inspection of the Wet Limestone Scrubbing Operation of the Kansas Power and Light Company

On February 10, 1971, the limestone scrubbing process unit at the Kansas Power and Light Company (KPL) was inspected by E. A. Burns. Discussions with Lee Brunton of KPL revealed this unit consists of marble bed scrubber of the effluent from the 115 megawatt coal fed (3.5% sulfur) combustion unit. In this unit limestone is injected dry into the combustor and the effluent particulate consists of 1.5% w/w going into the effluent pond of which half of that (0.75% w/w) consists of fly ash from the coal. Combustion Engineering, Windsor, Connecticut, is responsible for the sampling of this unit and grabs control samples at both the marble bed and the effluent pond. At one time they had experienced a serious calcium sulfate/sulfite scaling problem but this no longer is occurring; this problem was attributed to operational conditions at a relatively high pH (7.5-8.0). When the unit is operated in a recycle mode they have demonstrated 85% sulfur dioxide removal compared to a 60-70% removal without recycling. After discussions by phone with Jim Martin (Combustion Engineering), authorization was given to TRW to obtain samples of 1) the scrubber effluent going into the pond, and 2) the make-up water (that coming out of the pond after many days of settling). These samples were returned to TRW for characterization.

2.4 INSTRUMENTAL METHODOLOGY FOR CATIONS AND ELEMENTS

The list of elements in solution presented in Table I is of significance for determining the required process mass balance about a 20% sulfur closure. However, laboratory analysis of numerous other elements will undoubtedly be required in the forthcoming demonstration tests. The origin of these species are in the trace component variations in the coal, scrubbing agent and make-up water while the importance of their determination lies in understanding catalytic reactions or other spurious side effects. Table V delineates the elements of concern in their probable ion or compound forms.

TABLE V
POSSIBLE LIMESTONE/DOLOMITE SLURRY COMPONENT DISTRIBUTION[a]

Major Components		Minor Components	
Liquid Phase	Solid Phase	Liquid Phase	Solid Phase
Ca^{2+}	CaO	K^+	MPO_4
Mg^{2+}	MgO	PO_4^{3-}	SiO_2
HSO_3^-	$Ca(OH)_2$	NO_3^-	CaF_2
SO_4^{2-}	$Mg(OH)_2$	Na^+	PbS
H_2CO_3	$CaSO_3$	Fe^{3+}	Al_2O_3
HCO_3^-	$CaSO_4$	Fe^{2+}	S_8
$CaSO_4^\circ$	$CaCO_3$	Mn^{2+}	ZnS
	$MgCO_3$	Cl^-	Na_2O
		NO_2^-	MSO_4
		NO_3^-	FeS_2
		$S_2O_6^{2-}$	Fe_2O_3
		$S_3O_6^{2-}$	TiO_2
		$MgSO_3^\circ$	Co_2O_3
		$CaSO_3^\circ$	
		SO_3^{2-}	

Of the numerous laboratory methods referenced in Table II and Appendix A for the elemental analysis of slurry liquor and solids, two primary candidate instrumental methods met or exceeded the general criteria (Section 2.2) for selectivity, sensitivity, calibration, minimal sample preparation, speed of quantitative analysis, etc., i.e.:

- X-ray Fluorescence Spectroscopy (XRF), and
- Atomic Absorption Spectrophotometry (AA)

2.4.1 Laboratory X-Ray Spectroscopic Methodology

The X-Ray fluorescence (XRF) technique for quantitative laboratory analysis of elemental distribution, notably total sulfur, calcium, magnesium, as well as other metals, in slurry liquor and solids was evaluated primarily as an adjunct to process instrumentation development. The results of this study have, in addition, definitely identified XRF as one of the two recommended techniques for laboratory instrumental analysis. A concise review and recommendation of dispersive and non-dispersive X-Ray equipment is presented in Appendix D. Because of the emphasis on process instrumentation only those companies offering units amenable to process control were included in this effort. Consequently, the findings are not all inclusive for laboratory instruments because there are several other instrument manufacturers that may offer acceptable instruments.

The evaluation and development of the technique was accomplished through a review of pertinent literature, in-house experimentation, vendor contacts and experimental evaluation at vendor laboratories.

2.4.1.1 XRF Applications in Literature - Results of typical laboratory X-Ray analysis of limestone are listed in Table VI showing that excellent precision can be achieved with this instrumental technique.

TABLE VI

XRF ANALYTICAL DATA FOR LIMESTONE (REFERENCE 5)

Element	Kα Energy kev	Range % w/w	Conc. Found % w/w	Avg. Dev.* % w/w	Precision % w/w
Ca	3.69	35-52	41.2	0.36	±0.055
Al_2O_3	1.49	0.5-3	2.0	0.06	±0.057
SiO_2	1.74	0.5-30	10.8	0.26	±0.15
Fe_2O_3	6.4	0.5-1.5	0.95	0.01	±0.003
MgO	1.25	1-6	1.8	0.08	±0.08

***Average Duplicate Analysis - ARL VPXQ**

Comparison of X-ray fluorescence to standard wet chemical methods have been reported by Fabbi (Reference 6) (Table VII) for the single most important element that must be determined in the slurry solids - sulfur. Much additional statistical data are available that indicates the adequacy of the techniques in terms of sensitivity, accuracy and precision for sulfur and the other cations and metals of interest (Ca, Mg, Fe, Mn, V, Co, etc.).

TABLE VII

COMPARISON OF XRF AND CHEMICAL VALUES FOR TOTAL SULFUR IN STANDARDS AND MINERALIZED SAMPLES

		Sulfur (% w/w)		
No.	Rock Type	Total Sulfur by XRF	Total Sulfur by Na_2CO_3 Fusion[a]	Sulfur by Aqua Regia Solution[b]
1	Tuff or ash	0.01	0.00	...
2	Diabase	0.20	0.19	...
3	Tuff	1.03	1.16	...
4	Crush rocks adit	1.97	1.85	...
5	Altered quartz	2.42	2.52	...
6	Sulfidic phyllite	3.35	3.10	...
7	Sulfidic phyllite	4.97	4.97	...
8	Altered augite biotite monzonite	1.62	...	1.60
9	Augite biotite monzonite	0.07	...	0.07
10	Hybrid aplite	1.06	...	1.00
11	Hybrid pyroxenite	0.11	...	0.10
12	Hybrid aplite	0.79	...	0.80
13	Hybrid monzonite	0.64	...	0.64
14	Hybrid monzonite	0.08	...	0.16
15	Hybrid aplite	0.42	...	0.44
16	Hybrid aplite	1.10	...	1.20
17	Hybrid pyroxenite	0.18	...	0.16

[a] Analyses by conventional gravimetric methods. U.S. Geological Survey Analytical Laboratories under the direction of L.C. Peck

[b] Analyses by rapid methods. U.S. Geological Survey, Analytical Laboratories under the direction of L. Shapiro

2.4.1.2 XRF Analysis of Simulated and Field Samples - Prior to and concurrently with experimentation at vendor application laboratories (discussed below), numerous samples of simulated and actual field samples of starting limestone, fly ash, scrubber liquor, and scrubber solids were analyzed by XRF to demonstrate the applicability, accuracy and cost effectiveness of this technique. The instrument utilized at TRW for all in-house analyses was a

General Electric Model XRD-5 spectrometer. Samples were received directly from J. Barkley of TVA and consisted of simulated liquids and solids. Actual field samples of trapped solids from the Duke Power Company were submitted through R. M. Statnick, OAP Project Officer. Descriptions of samples, the analytical procedure and a discussion of results are presented in Appendix D.

It is noteworthy that the XRF analysis of several of the proposed specimens detected some errors in the assumed composition. In the case of calcium taken in solid samples identified as No. 1, No. 2 and No. 3, the calcium present in the added fly ash was not taken into consideration. Correction for the 8.51% calcium in the ash as determined by XRF gave relative erros of 1.5, 1.0 and 0.6% for calcium contents which ranged from 16% to 30% w/w. The value of the XRF technique was further exemplified when a discrepancy in the reported sulfur value taken versus that found was elucidated by interpretation of the XRF data. In essence, the analytical data were sufficiently precise and consistent to permit identification of the use of an anhydrous sulfate salt as opposed to a dihydrate salt as reported for sample preparation. Based on this postulation, relative errors for total sulfur were computed to be 6.6% (0.4% absolute), 1.6% and 0.

2.4.1.3 X-Ray Equipment Vendor Contacts - Literature on laboratory and process X-ray analysis equipment was requested from the following list of vendors:

ARL
Siemens
G. E.
Philips
JEOL Inc.
Picker

Information was received from each, however, only ARL and G.E. offered on-line process equipment. Consequently, within the constraints described previously, only their units have been evaluated in detail.

In the course of acquisition of information on available instruments, an alternative approach was identified which is capable of monitoring sulfur content and other elements in the wet scrubber operation. This alternative involves non-dispersive X-ray spectroscopy and utilizes radiation from radioactive sources (Fe, Cd, Am) as the primary source of excitation.

The following seven firms sell these instruments:

Canberra Industries, 45 Gracey Avenue, Meriden, Conn.
KEVEX Corporation, 898 Mahla Road, Burlingame, Calif.
Nuclear Equipment Co., 931 Terminal Way, San Carlos, Calif.
Nuclear Diodes, P. O. Box 135, Praire View, Ill.
ORTEC, 101 Midland Road, Oak Ridge, Tenn.
Panametrics, 221 Crescent St., Waltham, Mass.
Princeton-Gamma-Tech, Box 641, Princeton, N.J.

Of these, KEVEX and Nuclear Instruments were contacted for information on performance of their respective instruments. Several major points should be made:

- Sulfur can be detected with the isotope-activated non-dispersive systems. KEVEX personnel have demonstrated that 0.02% S in steel can be detected. Those experiments were admittedly performed under special conditions and it seems reasonable to expect useful analysis at 0.2% sulfur level under less than optimal conditions. Nuclear Equipment Company has used their standard system to determine that certain solid samples from the New York Air Pollution Control District contained 0.1% sulfur.
- A number of the units require liquid air refrigeration and cannot be allowed to warm up to room temperature. The samples need not be cooled.
- The units utilize 25-100 mC of radioactive material (Fe^{55}, Cd^{108}, Am^{241}) and require a license from the Atomic Energy Commission. The radioactive material does not mix with the slurry stream.
- The KEVEX Corporation instrument has an automated sample handling capability.
- Elements other than sulfur can be detected and in the ideal case, the lowest atomic number element that can be detected is #11 (sodium). For on-line slurry situations, sulfur may be the lowest atomic number detected.
- The energy selectivity of the non-dispersive system is an order of magnitude poorer than for other X-ray fluorescence techniques and could be a source of trouble in very complex samples that would offer no trouble to an ARL-type unit.
- The approximate costs of the non-dispersive units are from $14K to $28K depending on the type of data retrievable that is necessary.

As a consequence of these findings, additional consideration was given to the isotope activated non-dispersive X-ray spectrometer technique for monitoring of wet scrubber slurries.

2.4.1.4 Experimental Evaluation at Vendor Application Laboratories - For the purpose of evaluating instrumentation at the two selected vendor application laboratories, i.e., ARL and KEVEX, samples were prepared using pulverized fresh and spent scrubber solids as matrices together with known quantities of calcium sulfate and iron which were homogeneously cast into plastic resins which are substantially transparent to X-rays. Thus the particulate samples were frozen in solids at concentrations which are likely to be found in 1) dynamic scrubber samples of high and low concentrations or in 2) static samples which contain relatively low residual water content. The sample specimens consisted of a 1.25-inch diameter cylinder having a 0.125-inch thickness. The simulated slurry samples had the composition identified in Table VIII, which were prepared in either epoxy resin (in the case of the low solid concentration) or polyvinyl alcohol (in the case of the 99% solids loading).

At the Applied Research Laboratories at Sunland, California, the 14 listed samples were analyzed on an ARL X-ray Quantometer 7200. Although this instrument is a laboratory unit and only accomodates batch samples, it contains the same basic X-ray fluorescent spectrometer as the process unit (Model PCXQ) and, therefore, it served the dual purpose of evaluating both types of equipment.

A more complete description of the visit to the ARL Application Laboratory with a discussion of limits of detection, repeatibility, matrix effects, quantitative analysis, particle size effects and liquid cell signal attenuation is presented in Section 3.2, Continuous On-line X-ray Fluorescence Methods for Cations and Elements. The complete technical and economic evaluation of this instrument compared to G.E. and KEVEX instruments is presented in Appendix D. The ARL laboratory instrument was found to meet or exceed technical requirements of:

- Sensitivity - >0.1% for Ca, Mg, S and other elements of interest
- Precision - $\geq$2% of measured value

TABLE VIII
XRF STANDARD SAMPLES FOR INSTRUMENT EVALUATION

TRW Sample	Material	Form	Purpose or Function	Sulfur Content (% w/w)
001	$CaCO_3$	Dry	Standard for background	-
002	$CaCO_3$ + 7.9% $CaSO_4$	Dry	Determine detectability limit for sulfur	1.85 calculated[a]
003	$CaCO_3$ + 14.6% $CaSO_4$	Dry	Determine detectability limit for sulfur	3.44 calculated
004	Limestone	Dry	Standard for background	0.05 nominal wet chemical
005	Limestone + 7.9% $CaSO_4$	Dry	Detectability limit	1.87 calculated
006	Limestone + 14.6% $CaSO_4$	Dry	Detectability limit	3.44 calculated
007	$CaCO_3$ + 7.7% $CaSO_4$ + 0.9% Fe	Dry	Determine interference	1.81 calculated
008	Limestone/TVA-Flyash	Dry	Determine S/Ca ratio	1.765 wet chemical
009	Limestone/Zurn-Flyash	Dry	Determine S/Ca ratio	0.045 wet chemical
010	TVA-Flyash + 98% Epoxy	Dry	Effects of dilution	-
011	TVA-Flyash + 91% Epoxy	Dry	Effects of dilution	-
012	Zurn-Flyash 98.5% Epoxy	Dry	Effects of dilution	-
013	Zurn-Flyash + 91% Epoxy	Dry	Effects of dilution	-
014	$CaCO_3$ + 7.2% $CaSO_4$ + 7.2% Na_2SO_3	Dry	$SO_3^=$ - $SO_4^=$ resolution	3.43 calculated

[a] The calculated sulfur percent values are based on the known stoichiometric ratios in $CaCO_3$, $CaSO_4$, and Na_2SO_3.

Utilizing the XRF technique and an ARL lab unit it is estimated that approximately 1000 elemental analyses can be performed in an eight-hour shift by a single technician at a cost of ~$0.96/element. These specification time and cost factors are far superior to any other technique with the possible exception of the atomic absorption technique for liquids.

2.4.2 Atomic Absorption Spectrophotometric Methodology

Laboratory experiments were performed to evaluate and develop acceptable atomic absorption procedures (AA) for the rapid determination of calcium and magnesium primarily, but also other elements of concern such as sodium, potassium, iron, manganese, titanium, etc., in the scrubber slurry. The investigation was limited in scope to studies of the applicability for analysis of clarified or filtered slurry liquor exclusively. However, dissolution of solids with appropriate dilution is standard AA technique that requires more time in sample preparation but it can be equally applicable to the slurry solids for quantitative analysis in the absence of the recommended XRF capability.

Analyses were conducted utilizing a Perkin-Elmer Model 290 Atomic Absorption Spectrophotometer. It should be pointed out that significant instrumentation advancements have been made recently to yield much higher sensitivities, and more versatile units with multiple lamp turrets for more rapid element change over and to capability for simultaneous atomic absorption/atomic emission.

Of primary concern were 1) pH effects, 2) optimum fuel and oxidizer, and 3) effects of established methods of interference inhibition. The results of this study are delineated in Table IX. These findings show that calcium, in a solution made from saturated filtered limestone solution which has then been treated with a small amount of H_2SO_3 and finally adjusted with H_2SO_4 to pH 4 to 7, is stable in the burner flame.

Best results were obtained by using a lanthanum inhibitor and acetylene/N_2O flame. At pH 2, absorption decreases to an unreliable reading even when the inhibitor is used. The literature indicates that this effect is produced not by the increased acidity as such, but by a change in the viscosity and surface tension of the solution. This, in turn, produces a decrease in atomizer efficiency resulting in inaccurate response.

TABLE IX

EFFECT OF FLAME OXIDIZER, pH AND INHIBITOR ON ATOMIC ABSORPTION DETERMINATION OF CALCIUM IN LIMESTONE SOLUTIONS[a]

Solution pH	Acetylene/Air Flame With Inhibitor Calcium Found % w/w	Acetylene/N_2O Flame with Inhibitor Calcium Found % w/w	Acetylene/N_2O Flame Without Inhibitor Calcium Found % w/w
9.5	0.01	0.02	0.01
7	0.02	0.026	---
6	0.021	0.026	0.026
4	0.02	0.026	---
2	---	0.011	0.0006

[a] Analytical calcium concentration taken = 0.026 % w/w

Typical suspect constituents present in filtered slurry samples obtained from the operational limestone wet scrubber units described above, were analyzed by atomic absorption spectrometry. The results of these tests are reported in Table X.

TABLE X

ATOMIC ABSORPTION ANALYSIS OF SELECTED SAMPLES OBTAINED FROM OPERATIONAL LIMESTONE WET SCRUBBER UNITS

Element	Zurn Feed Slurry Liquor ppm	Zurn Spent Slurry Liquor ppm	KPL Spent Slurry to Clarifier ppm	KPL Make-up Liquor from Clarifier ppm
Magnesium	4000	2700	<0.01	0.4
Calcium	435	1088	1360	340
Sodium	10800	6800	1500	1200
Potassium	420	420	20	8.2
Copper	0.35	0.10	<0.05	<0.05
Mercury	<4.0	<4.0	<4.0	<4.0
Iron	<0.1	<0.1	<0.1	<0.1
Nickel	<0.2	<0.2	<0.2	<0.2
Chromium	<0.05	<0.05	<0.05	<0.05
Manganese	0.02*	0.16	<0.02*	<0.02
Aluminum	<1.6	<1.6	<1.6	<1.6
Titanium	<5.0	<5.0	<5.0	<5.0

*1 div ~ limit of detection of instrument utilized

For the purposes of further evaluating the AA technique (as well as the other candidate methods presented in subsequent sections of this report), a simulated, static liquid slurry was prepared from reagent chemicals and deionized water. The added quantities of anions and cations are delineated below together with found concentrations in solutions.

Constituent	Added (ppm)	Found (ppm)	Constituent	Added (ppm)	Found (ppm)
Ca^{2+}	1000	480 (12*mM*)	K^{+}	450	450 (11.5*mM*)
Mg^{2+}	1040	1040 (43*mM*)	Na^{+}	200	200 (8.7*mM*)
Fe^{3+}	25.0	$\leq$0.1	Ni^{2+}	1.0	0.1
Cu^{2+}	1.1	$\leq$0.05	SO_4^{2-}	6400	5828 (61*mM*)
Mn^{2+}	1.2	1.2	NO_3^{-}	570	570 (9.2*mM*)
Al^{3+}	5.2	$\leq$1.6	Cl^{-}	60	60 (1.7*mM*)
Fe^{2+}	25.2	$\leq$0.1	CO_3^{2-}	500	315 (5.2*mM*)

All found cation values were determined utilizing the P-E Model 290 AA unit. Excellent correlation was found for the more soluble species Mg, Mn, K and Na, adding further credance to the arguments in favor of the AA technique over other proposed techniques, especially the manual EDTA titration methods. The anion determinations were performed by the standard methods described in Sections 2.6 - 2.8. The apparent mass balance discrepancies can be explained by partial precipitation of some of the species by carbonate, sulfate and hydroxide species. Although no single AA instrument can be recommended for this application, the following candidate companies are suggested as a minimum list for consideration.

Bausch & Lomb
Beckman
Corning
Instrument Laboratories
Varian
Jarrel Ash
Perkin-Elmer
Spectra Metrics
Technicon

2.5 SPECTROPHOTOMETRIC ANALYSIS OF SULFITE AND BISULFITE

Sulfite ion or the S(IV) species in solution was identified early in the program as one of the major species to be determined in 1) assessing process efficiency and optimization and 2) the performance of a mass balance about sulfur. In several wet scrubbing processes the ratio of sulfite to sulfate is critical to the economics of the process in terms of reagent regeneration or ultimate product synthesis for scrubbing process credit.

During the review of candidate laboratory analytical methods for the determination of dissolved sulfur dioxide as HSO_3^- and $SO_3^=$, it was determined that no satisfactory instrumental methods existed for 1) determining the anticipated concentrations (Table I) in the limestone slurry mixtures, or 2) met the general criteria of speed, accuracy, automatability, adaptability to routine operation by semi-skilled operators and use of relatively low cost equipment. One other important aspect in considering candidate methods was the likelihood of successful development and implementation of the method by January 1972.

Experimental or theoretical evaluation studies of several spectrophotometric methods including methods based on direct sulfite absorbance, pararosaniline, fast blue salt, fuchsin-aldehyde, 5-aminofluoroescein and furfural. As a result of this evaluation the furfural method was deemed to offer the best potential for meeting the above criteria and indeed, a new method based on bisulfite bleaching of the furfural UV absorption was developed. This method is based on the chemical reactions in Equations 1 - 4 and depends on the bleaching of the 276 *nM* absorption of furfural by reaction with bisulfite.

$$C_4H_3OCHO + HSO_3^- \rightleftarrows C_4H_3OCHOHSO_3^- \quad (1)$$

$$C_4H_3OCHOHSO_3H \rightleftarrows C_4H_3OCHOHSO_3^- + H^+ \quad (2)$$

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^- \quad (3)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^= \quad (4)$$

The absorbance, A, at 276 *nM* is directly related only to the amount of furfural in solution when the pH of the media is maintained around 4.0 in accordance with the Lamber-Beer-Bouguer Law.

$$A = abc_F \quad (5)$$

where a = molar absorptivity of furfural, liters/mol-cm
b = optical path length, cm
c_F = concentration of uncombined furfural, *M*

The equation of the bleaching reaction (Equation 1) is governed by the formation constant, K

$$K = \frac{c_A}{c_F[HSO_3^-]} \qquad (6)$$

where c_A = concentration of furfural-sulfite adduct, *M*

$(c_A = c_o - c_F)$

$[HSO_3^-]$ = concentration of uncombined bisulfite, *M*

c_o = analytical concentration of bisulfite taken, *M*

Combining Equations 5 and 6 results in a relationship of absorbance and bisulfite ion as shown in Equation 7.

$$\frac{1}{A} = \frac{K}{abc_o}[HSO_3^-] + \frac{1}{abc_o} \qquad (7)$$

Consequently, the function of 1/A is linearly proportional to the free bisulfite concentration; also, the formation constant can be calculated from the ratio of the slope to intercept of the straight line relationship. It is interesting to note that this method was first developed for the determination of furfural and prior to this study has not been used for the determination of bisulfite (Reference 7). The reason for this is because in most situations colorimetric procedures are used for determining low concentrations of chemical species but in the limestone scrubber case the concentration of bisulfite (1-150 *mM*) is too large for trace analysis methods (without massive dilution) and not readily adaptable to common macro titrimetric procedures (without using large volumes and dilute titrants).

Detailed studies of the effect of pH, diverse ions, temperature and time to constant color development are described below. The effort has culminated in a rapid, simple instrumental method which can utilize a single reagent condition consisting of furfural, phosphate buffer and sulfamic acid (to remove trace concentrations of nitrite interference). The reproducibility of the method has been determined to be better than 2% relative or 0.2 *mM* absolute whichever is higher. The formalized procedure in a format geared to chemical technician implementation is presented in Appendix E.

2.5.1 Effect of pH

As the furfural bleaching was reported to be a direct function of complexation by the bisulfite ion (Equation 1 above), it was necessary to maximize the bisulfite concentration through pH control and determine the effect of varying pH on the reaction equilibria. The relative concentrations of sulfur (IV) species, i.e., undissolved sulfurous acid, bisulfite ion and sulfite ion, as a function of pH are shown in Figure 2. Based on the bisulfite curve, it was originally postulated that pH control in the region of approximately pH 3.5 to 5.0 would be useful for analytical purposes. The actual optimum pH range was determined experimentally and is described below.

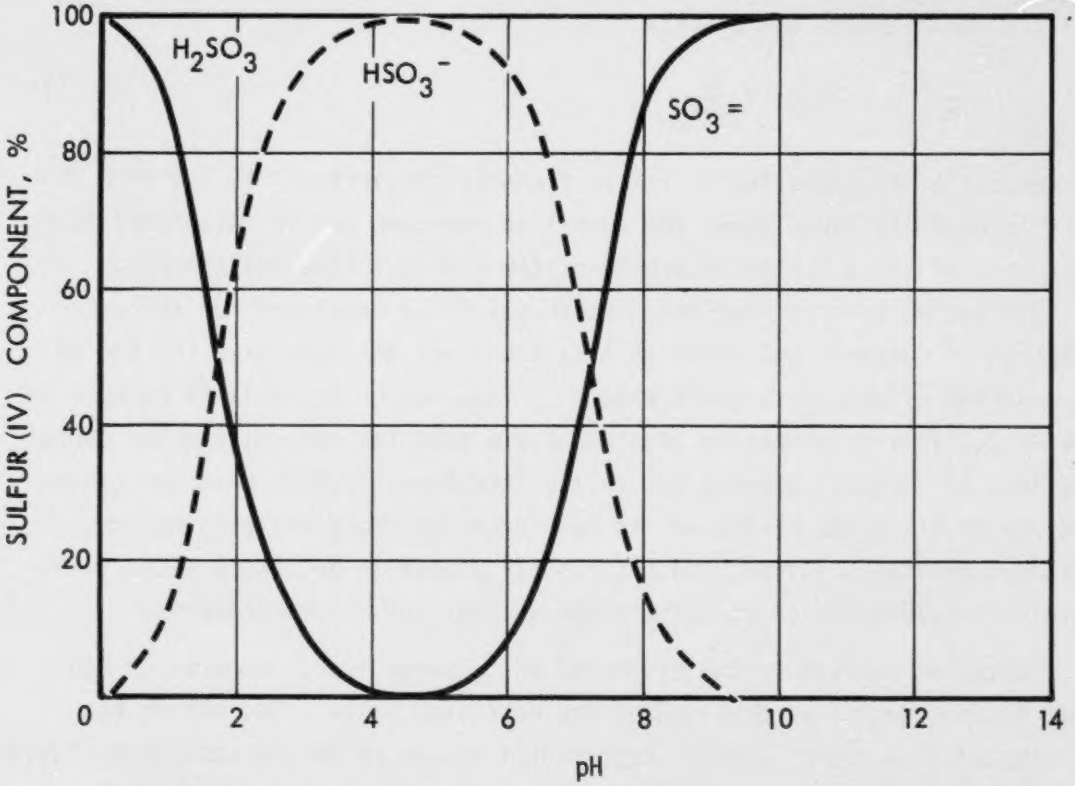


Figure 2. Sulfur IV Species as a Function of pH

Two principal buffer systems were evaluated, i.e., acetate-acetic acid and phosphate-phosphoric acid. Prior to determining the effect of pH on sulfite determination, the effect of pH on the absorbance of neat furfural (baseline) was investigated. The results of these tests are shown in Table XI.

TABLE XI
pH DEPENDENCE OF FURFURAL ABSORPTION SPECTRUM AT 276 *nM*[a]

pH	Absorbance	Buffer System
7.88	0.777	-
6.94	0.775	-
6.52	0.772	-
6.40	0.768	-
4.24	0.760	Phosphate-Acetate
4.24	0.760	Phosphate
3.70	0.758	Phosphate
3.51	0.767	Phosphate
2.80	0.772	Phosphate

[a] Concentration of furfural = 50.7 μM

It is interesting to note that an apparent minima occurs in the absorbance of furfural in the 3.7 - 4.3 pH range. Although the differences are small, the monotonic nature of the curve lends credence to the belief that the effect is real. As a consequence, it appeared desirable from both the stability of the furfural absorption and the major effect on ensuring the maximum bisulfite S(IV) form to definitize further the optimum pH range for the furfural bleaching method.

Utilizing reagent grade sodium bisulfite in an unbuffered system, absorbance versus concentration of S(IV) gave the data in Table XII. The least squares plot for these data gave

$$1/A = 2.359C + 1.349 \qquad (8)$$

Where C = analytical concentration of bisulfite millimolar (*mM*)

The values listed for bisulfite found were obtained by Equation 8. Linearity deteriorated appreciably for bisulfite concentrations greater than 2.25 *mM*. The sulfite concentration range of interest (Table I) was identified from equilibrium calculations to be 1 to 150 *mM*. Consequently, it will be necessary to dilute the scrubber liquor to a point in which the bisulfite content does not exceed 2.25 *mM* to obtain reliable results.

TABLE XII

DETERMINATION OF BISULFITE BY FURFURAL BLEACHING IN UNBUFFERED MEDIA

Bisulfite[a] Taken *mM*	Final pH	Absorbance (A)[b]	1/A	Bisulfite Found *mM*	Deviation *mM*
0.000	6.94	0.776	1.228	-0.023	-0.023
0.106	5.25	0.643	1.555	0.090	-0.010
0.211	4.70	0.541	1.848	0.214	+0.003
0.317	4.40	0.478	2.09	0.316	-0.001
0.422	4.30	0.427	2.34	0.422	0.000
0.528	4.12	0.383	2.61	0.536	+0.008
0.845	3.96	0.295	3.39	0.866	+0.021
1.06	3.93	0.257	3.89	1.08	+0.020
1.12	3.80	0.245	4.08	1.16	+0.040
2.11	3.60	0.163	6.13	2.03	-0.080
2.25	3.3	0.148	6.75	2.29	+0.040

[a] Solutions prepared by dilution of stock sodium bisulfite solutions (acidified to give pH = 3.1)

[b] The analytical concentration of furfural in the final solution was 50.7 *μM*

The results of analysis of standard sodium bisulfite solution using the sodium acetate/acetic acid buffer system are tabulated in Table XIII. As can be seen, excellent precision was obtained in the 3.6 to 3.9 pH range. The sodium dihydrogen orthophosphate/phosphoric acid buffer permitted extension of the furfural-bisulfite method into the pH 4 region, thus, together with the acetate system, allowing pH control through the theoretically useful range of the technique.

The determination of bisulfite by furfural bleaching in the phosphate buffer system was performed at two pH regions, 3.6 and 4.4 with the combined results listed in Table XIV. The furfural concentration in these experiments was 50.1 *μM* and the bisulfite content was varied between 0.2 and 2.3 *mM*. The relationship between absorbance and bisulfite content for this data is given by the following expression which is an average of the two sets of constant pH data:

$$1/A = 2.522C + 1.329 \qquad (9)$$

The significant differences between Equations 8 and 9 clearly point out the need for measurement in a buffered (constant pH) media.

TABLE XIII

DETERMINATION OF SULFUR (IV) BY FURFURAL BLEACHING

Sulfur (IV) Taken[a] *mM*	pH[b]	Absorbance (A)[c] at 276 *nM*	1/A	Sulfur (IV) Found *mM*	Deviation *mM*
0.000	3.9	0.760	1.315	0.001	+.001
0.101	3.9	0.643	1.555	0.100	-.001
0.202	3.8	0.559	1.789	0.196	-.006
0.306	3.7	0.483	2.07	0.311	+.005
0.407	3.7	0.437	2.29	0.401	-.006
0.509	3.6	0.388	2.58	0.520	+.011
0.814	3.6	0.303	3.30	0.815	+.001
1.020	3.6	0.264	3.79	1.016	-.004

[a] Added from stock sodium sulfite solutions, concentrations listed are those of diluted analyzed solutions.

[b] A sodium acetate - acetic acid buffer was utilized for pH control.

[c] The analytical concentration of furfural in final solution analyzed was 50.7 *µM*

where C is the concentration of bisulfite (*mM*), the intercept is 1.329 (similar to that obtained for the acetate buffered system) and the slope is 2.522. The slope for the acetate buffered system was 2.439. This equation was used to calculate the values for bisulfite found in the table. The effect of pH ∿3.6 and pH ∿4.4 can be evaluated by treating the data as two separate sets of data as shown in Table XIV. The least squares equations and the errors about the equations are listed. At pH ∿3.6,

$$1/A = 2.527C + 1.346 \tag{10}$$

while at pH ∿4.4,

$$1/A = 2.513C + 1.305 \tag{11}$$

The significance of the difference between these equations and the equation (9) derived from the composite data has been evaluated by statistical treatment of the errors. The significance of the differences was tested by comparison of the variance ratio (or F test) of the pooled variance of the two equations with the variance of the composite equation.

TABLE XIV

EVALUATION OF pH EFFECT IN DETERMINATION OF S(IV) IN PHOSPHATE BUFFER

Bisulfite Taken [*mM*]	pH	Absorbance(A) at 276*nM*	1/A	Bisulfite Found [*mM*]	Deviation [*mM*]	Relative Error(%)
0.000	3.5	0.763	1.311	0.014	+0.014	1.4
0.227	3.5	0.529	1.890	0.215	-0.012	5.3
0.511	3.5	0.379	2.634	0.512	+0.001	0.2
0.511	3.7	0.377	2.653	0.517	+0.006	1.2
1.520	3.5	0.190	5.263	1.550	+0.030	2.0
1.520	3.7	0.190	5.263	1.550	+0.030	2.0

$$1/A = 2.527C + 1.346(\pm 0.00476) \qquad (10)$$

Variation for intercept = 0.00166
for slope = 0.00112

Bisulfite Taken [*mM*]	pH	Absorbance(A) at 276*nM*	1/A	Bisulfite Found [*mM*]	Deviation [*mM*]	Relative Error(%)
0.000	4.2	0.760	1.316	0.004	+0.004	0.4
0.194	4.3	0.557	1.795	0.195	+0.001	0.5
0.437	4.3	0.421	2.375	0.425	-0.012	2.7
1.500	4.5	0.196	5.102	1.511	+0.011	0.7
2.230	4.6	0.145	6.897	2.225	-0.005	0.2

$$1/A = 2.513C + 1.305(\pm 0.000604) \qquad (11)$$

Variation for intercept = 0.000245
for slope = 0.000165

Standard deviation = 0.0246

The variances for the individual and pooled data are as follows:

at pH 3.6: $S^2_{xy} = .00476$ @ 5 d.f.

at pH 4.4: $S^2_{x-y} = .000604$ @ 3 d.f.

$$S^2_p = \frac{(5 \times .00476) + (3 \times .000604)}{8} = 0.0032 \text{ @ 8 d.f.}$$

For all data, the variance is:

$$S^2 = 0.00345 \text{ @ 10 d.f.}$$

Thus, the ratio gives:

$$F_{8,10} = \frac{.00345}{.0032} = 1.08$$

which is not significant at the 99% confidence level.

Using the two buffer systems (acetate and phosphate) and combinations, where necessary, an experimental curve of bisulfite concentration versus pH was obtained. For each point on the curves, the solutions containing 1.0*mM* and 0.5*mM* bisulfite and $5 \times 10^{-5}M$ furfural were adjusted to the desired pH with the appropriate buffer and the furfural absorption (A) measured at 276 *m*μ. Because the term 1/A is directly proportional to bisulfite concentration, the shape of the 1/A vs. pH curve (Figure 3) provides a measure of the useful pH range (at maximum 1/A), as well as the effect of small pH variations on bisulfite determination in this range.

The experimental curve for the 1 *mM* concentration of HSO_3^- compares favorably with a theoretical best fit curve generated by computer for the idealized quadratic equation:

$$y = a + bx - cx^2 \tag{12}$$

Examination of the curve and experimental and computed 1/A values together with the relative error, listed in Table XV, indicates excellent agreement with the theoretical curve (Figure 3). Assuming a maximum experimental relative error of ±3% in the pH region of maximum bisulfite concentration, the usable analytical pH range extends from 3.5 to 4.5. One can infer from Figure 3 that the method may be applicable to the determination of HSO_3^- in $HSO_3^- - SO_3^=$ mixtures, however, the accuracy of the measurement at low HSO_3^- concentration plus the apparent pH dependency of molar absorptivity preclude the use of the method for this determination.

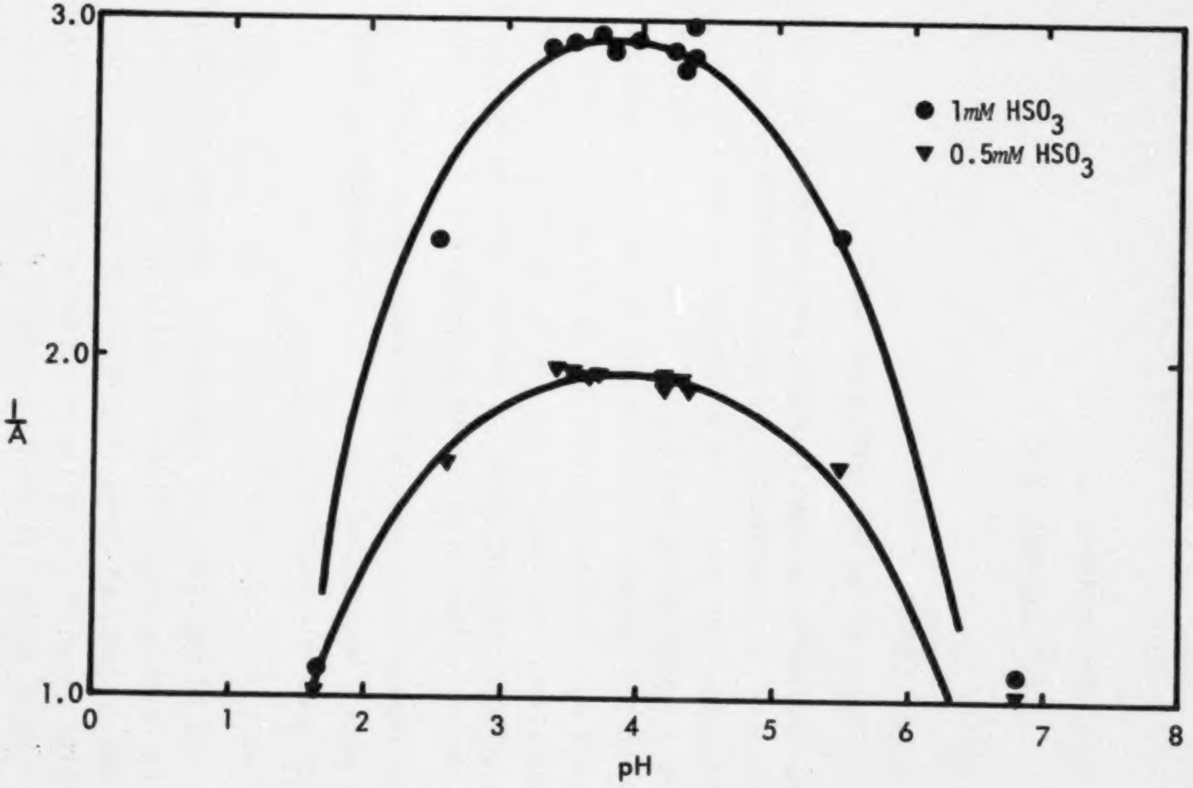


Figure 3. Bisulfite-Furfural Absorption as a Function of pH

TABLE XV

EXPERIMENTAL AND COMPUTED pH VERSUS 1/A(HSO_3^-)

pH	1/A	$1/A_c$	Deviation in 1/A	Relative Error, %	
1.66	1.0740	1.2189	+0.1449	13.5	
2.52	2.3536	2.2171	-0.1365	5.8	
3.35	2.9378	2.7893	-0.1485	5.1	
3.53	2.9483	2.8627	-0.0856	2.9	Useful range
3.73	2.9768	2.9231	-0.0537	1.8	
3.80	2.9088	2.9389	+0.0301	1.0	
4.00	2.9429	2.9692	+0.0263	0.9	
4.25	2.9151	2.9757	+0.0606	2.1	
4.34	2.8701	2.9694	+0.0993	3.4	
4.40	2.9018	2.9628	+0.0610	2.1	
4.40	2.9880	2.9628	-0.0252	0.8	
5.50	2.3704	2.4853	+0.1149	4.8	
6.85	1.0604	0.9771	-0.0833	7.8	

$$y = a + bx - cx^2$$

$$y = -1.874 + 2.326\ x - 0.2788\ x^2$$

2.5.2 Effect of Diverse Ions and Total Ionic Strength

The effect of diverse ions expected to be present in the wet scrubber filtered liquors on the bisulfite-furfural bleaching method was investigated. The results of these screening studies are shown in Table XVI at relatively high additive concentrations.

Threshold interference level of that concentration of species causing an absorbance deviation greater than 3% relative from an identical sample without the interferent was used to define a positive interference. Calcium, magnesium, sodium, nickel, copper and manganese ions were determined to be non-interfering at concentrations expected in the wet scrubber media. The following threshold values were determined experimentally for Fe^{+++}, Fe^{++} and NO_2^-:

Species	Interference Level, *mM*[a]
Fe^{+++}	0.001 - 0.01
Fe^{++}	≥ 0.01
NO_2^-	≥ 0.01

[a] Concentration in the final diluted analytical sample where the S(IV) concentration is optimally on the order of 1 *mM*, the furfural concentration is 0.1 *mM* and pH is adjusted to 4.0 with phosphate buffer.

TABLE XVI

INTERFERENCE SCREENING TESTS FOR BISULFITE-FURFURAL BLEACHING[a]

Bisulfite Concentration *mM*	Additive		Absorbance[b]
	Compound	Concentration *mM*	
0.00	-	-	0.755
0.00	$CaSO_4$	0.0367	0.769
0.00	$MgSO_4$	10.20	0.765
0.00	NaCl	9.00	0.767
0.00	$Fe(NO_3)_3$	9.75	>2.0
0.00	$NaNO_2$	10.50	0.850
0.528	-	-	0.408
0.528	$CaSO_4$	0.0367	0.398
0.528	$MgSO_4$	10.20	0.392
0.528	NaCl	9.00	0.392
0.528	$Fe(NO_3)_3$	9.75	>2.0
0.528	$NaNO_2$	10.50	0.831

[a] Unbuffered

[b] Analytical concentration of furfural = 50.7 *μM*; absorbance at 276 *mμ*

Carbonate was added as sodium bicarbonate, and nitrate was added as potassium nitrate to evaluate potential interference from those components. Neither species at an unrealistically high 1*M* concentration caused a measurable deviation. Ionic strength* was investigated through the range 0.217*N* to 1.519*N* by varying the phosphate buffer concentration. As with the carbonate and nitrate, no interference could be detected and therefore these slurry components were deleted from further consideration. Nitrite, iron II and iron III, on the other hand, caused sufficiently severe perturbation to the analytical accuracy that further study and corrective action was necessary.

2.5.2.1 Elimination of Nitrite as an Interferent - The nitrite interference level cited above is considered to be a realistic concentration that can be encountered from absorption of NO_x from the flue gas. The NO_x consists of mixtures of nitric oxide and nitrogen dioxide. There appears to be little affinity for NO absorption in the limestone scrubber, however, NO_2 will react quantitatively with water by disproportionation to give equimolar quantities of nitrite and nitrate. At elevated temperatures nitrite can undergo further disproportionation to give nitrate and nitric oxide. The extent of these reactions that occur concurrently during the sulfur dioxide abatement process will depend on actual temperatures, concentrations, and residence times. The need for control of the nitrite interference becomes quite evident from examination of the following data:

NO_2^- ($NaNO_2$) Conc., m*M*	% Deviation from Control Absorbance
0.01	4
0.1	12
1.0	93

The compounds sodium azide and sulfamic acid were selected as candidate additive reagents for elimination of the interference in the furfural-bisulfite complex absorbance exhibited by nitrite ions. The reactions of these compounds with nitrite are as follows:

---

* $\mu = 1/2\ \Sigma\ (m_i \times z_i^2)$

$$NaN_3 + HNO_2 \rightarrow N_2 \uparrow + N_2O + NaOH \qquad (13)$$

$$NH_2SO_3H + HNO_2 \rightarrow N_2 \uparrow + H_2SO_4 + H_2O \qquad (14)$$

The azide reagent, however, was found to be ineffective as a supressant. Actually it caused a greater error in the method than the nitrite ion. Sulfamic acid, on the other hand, was shown to be effective as the nitrite interferant suppressant from the data in Table XVII.

TABLE XVII

EFFECT OF SULFAMIC ACID ON NITRATE INTERFERENCE

Furfural, μ*M*	HSO_3^-, *mM*	NO_2^-, *mM*	Sulfamic Acid, *mM*	A
50.24	-	-	-	0.777
50.24	1.0	-	-	0.281
50.24	1.0	0.10	-	0.352
50.24	-	-	1.2	0.778
50.24	-	-	0.6	0.775
50.24	-	-	0.1	0.779
50.24	1.0	-	1.2	0.289
50.24	1.0	-	0.6	0.278
50.24	1.0	-	0.1	0.278
50.24	1.0	0.10	1.2	0.286
50.24	1.0	0.10	0.6	0.293
50.24	1.0	0.10	0.1	0.275

No apparent change occurred in the furfural absorption or the furfural-bisulfite absorption upon addition of sulfamic acid at concentrations from 10^{-4} to $10^{-3}M$. From the table it can be seen that the increase in furfural absorbance (HSO_3^- present) upon addition of 10^{-4} *M* nitrite is ∿25% and upon addition of sulfamic acid in the concentration range from 10^{-4} to 10^{-3} *M* that this interference is essentially eliminated. The addition of sulfamic acid has been incorporated into the procedure as a standard precautionary measure.

2.5.2.2 Iron as a Potential Interferent - Iron is a significant constituent of coal burning power plant flue gas fly ash and can be found as a minor constituent in limestone. As the pH of the scrubber liquor varies so will the iron solubility and the potential for interference. Assuming some degree of solubility, the 276 *nM* absorbance of solutions containing phosphate buffer (pH ∿4.2), 1.0 *mM* bisulfite and a furfural concentration of 0.10 *mM*, was measured as a function of ferric ion concentration, added as ferric nitrate. Table XVIII shows the results of the ferric study.

TABLE XVIII

INTERFERENCE OF Fe^{+3} IN THE FURFURAL-BISULFITE METHOD[a]

Bisulfite conc., *mM*	Fe^{+3} conc., *μM* $Fe(NO_3)_3$	Absorbance	%Deviation
1.000	-	0.464	-
1.000	0.10	0.460	-0.9
1.000	1.0	0.472	+1.7
1.000	10.0	0.490	+5.6
0	10.0	1.412	+2.5
0	0.0	1.378[b]	-

[a] Phosphate buffer, pH 4.2 [b] Furfural conc. = 100.0 *μM* ∿ A = 1.378

Deviations in the absorbance of the furfural-bisulfite complex begin to become significant at concentrations greater than 10 *μM* ferric ion (+1.7% deviation at 0.001 *mM*). Ferric ion was found to interfere with the furfural absorbance alone, without HSO_3^- present, as well as with the complex. The significance of this potential interference is discussed below.

The aqueous chemistry of ferric iron affords a plausable explanation of the above observed interference. Ferric ion in aqueous solution has a strong tendency for hydrolysis and/or complex formation. The aquo ion that is formed will hydrolyze significantly at pH's in the range of 2-3, as indicated by the following equilibrium equations and constants:

$$[Fe(H_2O)_6]^{3+} = [Fe(H_2O)_5(OH)]^{2+} + H^+;\ K = 8.9 \times 10^{-4} \qquad (15)$$

$$[Fe(H_2O)_5(OH)]^{2+} = [Fe(H_2O)_4(OH)_2]^+ + H^+;\ K = 5.5 \times 10^{-4} \qquad (16)$$

At pH's greater than 2-3, condensed species are formed and eventually colloidal gels appear. For alkaline pH's ferric ion will become insoluble as the hydrous Fe_2O_3 is precipitated.

The aqueous UV absorption spectrum, which is believed to arise from the condensed forms of the hydrolyzed aquo complex, shows an intense charge transfer band in the far ultraviolet which exhibits a tail extending into the visible region of the electromagnetic spectrum. This tailing effect is present at 276*nM*: the analytical wavelength in the furfural bleaching method and hence, gives rise to increased absorbance values.

The efficacy of several complexing agents for the elimination of the iron (II and III) interference by measuring the molar absorptivities of the complexes at 276*nM* was investigated. The results were as follows:

Component Mixture	a(276 *nM*)*
Aqueous Fe^{3+}	3,200
Fe^{3+} - EDTA	5,400
Fe^{3+} - citrate	4,200
Fe^{3+} - tartrate	4,110
Fe^{3+} - Phosphate buffer	4,000
Aqueous Fe^{2+}	600
Fe^{2+} - EDTA	7,800
Fe^{2+} - citrate	1,200
Fe^{2+} - tartrate	600
Fe^{2+} - phosphate buffer	600

*Liter/mol-cm

It is readily apparent from the data that the interference of the aquo ferric iron complex is significant and that a bathochromic shift occurs for the charge transfer bands in the presence of the complexing agents. The increase in molar absorptivity of the complexed species precludes the use of complexing agents for the elimination of ferric ion interference.

Ferrous ion exhibits a lesser interference except in the presence of strong complexing agents such as EDTA or citrate ion. Thus, the addition of complexing agents to the scrubber solution would compound the interference if iron is present in the Fe (II) state.

The impact of the apparent iron problem becomes negligible, however, if the scrubber is operated in the planned pH range of 6.5 to 7.5. In this pH range the iron will be present in the condensed form as colloidal suspensions and would be removed by solid liquid phase separation techniques. In the simulated static slurry described in Section 2.4.2, Fe^{+3} and Fe^{+2} were added at a 25 ppm level (0.45 *mM*), but after filtration (Whatman No. 41) no iron could be detected in solution by atomic absorption spectrophotometry. It appears that efficient removal of colloidal species will be essential to the elimination of iron interference. In the event the scrubber is operated at a more acidic pH (3-4.5), it will be necessary to adjust the pH of the analytical liquor sample to neutrality and, after allowing sufficient time for nucleation, refilter the sample. It may be more expedient to utilize a cation exchange procedure for this purpose. This contingency is noted in the standard method, Appendix E.

2.5.3 Time Dependence of the Furfural-Bisulfite Complex Formation

In order to achieve automation of the furfural technique for the analysis of sulfur species, one of the basic criteria for selecting a method for development, a series of experiments were conducted to determine the parameters affecting time to equilibrium for the formation of furfural-bisulfite complex. The experiments were conducted on a Beckman DK-2A ratio recording spectrophotometer utilizing the time drive mode of operation and a constant temperature cell holder.

From examination of the results of the experiments, given in Table XIX it is apparent that the time dependence for complex formation is effected by temperature, concentration of bisulfite, concentration of furfural and pH. It is surprising, however, that the strongest dependence is on the pH of the solution. An attempt to fit the data to pseudo first order (large excess of HSO_3^-) and second order kinetic plots were unsuccessful which is indicative of complex solution kinetics.

At first glance the kinetics would be expected to follow second order equations for the reaction of one furfural molecule with a molecule of bisulfite. This, however, does not reflect the strong dependence of the kinetics on the solution pH. For the system under consideration it would

TABLE XIX
TIME DEPENDENCE ON THE FURFURAL-BISULFITE EQUILIBRIUM

Temperature (°C)	HSO_3^- (*mM*)	Furfural (*mM*)	pH	Time to Equilibrium (Min)
22	0.1	0.06	3.7	10.5
	0.5			9.5
	1.0			7.2
	1.5			5.8
22	0.1	0.06	3.9	8.0
	0.5			6.5
	1.0			4.5
	1.5			3.5
22	0.1	0.06	4.1	5.5
	0.5			5.0
	1.0			4.0
	1.5			2.8
22	0.1	0.12	3.9	7.0
	0.5			5.8
	1.0			4.6
	1.5			3.6
39	0.1	0.06	3.9	6.0
	0.5			5.5
	1.0			4.5

appear that the sulfurous acid-bisulfite and/or the bisulfite-sulfite acid base equilibria also participate in the reaction kinetics. This participation could yield additional terms in the rate expression resulting in a strong pH dependence.

The dependence of the reaction rate on pH will be utilized in the automated procedure to shorten the reaction times and yield minimum instrument hold times. Independent operating parameters include furfural concentration, bisulfite concentration, pH and temperature. For the automated procedure, furfural concentrations will be limited by available detection techniques and because bisulfate concentration is the variable to be determined, increased temperature, though not as effective in enhancing rates as the pH, will be used for enhancement. It is believed that by judicious selection of temperature and constancy in the rate of color development curve would permit analyses after 5-6 minutes at a nominal pH of 4.0.

2.5.4 The Effect of Temperature on the Furfural-Bisulfite Analysis

This section describes the study undertaken to determine the temperature dependence of the bisulfite calibration and the extent of control required to meet the specified accuracy. The studies employed a Beckman DK-2A spectrophotometer fitted with a constant temperature cell holder. To investigate the temperature effect, bisulfite calibration curves were run at temperatures of 21.0°, 35.0° and 62.2°C. Temperatures were recorded utilizing a chromel-alumel thermocouple immersed in the spectrophotometric cell liquid immediately proceeding measurement of each data point.

As previous reported the linear portion of the bisulfite calibration curve follows Equation 7, and the equilibrium constant K for the complex format ion may be determined by:

$$K = \frac{\text{Slope of the calibration curve}}{\text{Intercept of the calibration curve}} \qquad (17)$$

Changes in K with temperature are indicative of the temperature sensitivity of the analytical procedure. Additionally, because K represents an equilibrium constant for the formation of the complex a logarithmic plot of K versus 1/T would be expected to be linear and allow evaluation of temperature effects at any point within the range of temperatures investigated.

Calibration curves were obtained at three temperatures and are presented in Table XX. Six point calibrations were obtained for the experiments at 21.0° and 35.0°C, while only four calibrations were used at 62.2°C. A least squares evaluation of the data gave the following values for the equilibrium constants:

Temperature, °C	K (liter/mol)
21.0	1,800
35.0	740
62.2	141

A graphical presentation of ln K versus 1/T is shown in Figure 4. The resultant graph yields a straight line of slope 1.65×10^{-4} and intercept 2.16×10^{-3} (1/T, Y axis and ln K, X axis).

Because the calculated concentration of bisulfite for a given absorbance is inversely proportional to the equilibrium constant, the temperature

TABLE XX

THERMAL DEPENDENCE OF THE BISULFITE CALIBRATION CURVE

Temperature (°C)	HSO_3 Conc. [*mM*]	1/A
21.0	-	1.385
	0.185	1.818
	0.370	2.222
	0.555	2.632
	0.740	3.145
	0.925	3.584
35.0	-	1.445
	0.185	1.653
	0.370	1.852
	0.555	2.049
	0.740	2.252
	0.925	2.449
62.2	-	1.540
	0.186	1.560
	0.371	1.600
	0.558	1.640

effect resulting in a 5% error may be evaluated. Calculations show that the 5% error band is 1.2°C (or 2.2°F). The bisulfite calibration is sensitive to temperature fluctuations and thermal control is required.

2.6 INSTRUMENTAL ANALYSIS OF SULFATE

As in the case above for accurate, rapid and frequent determination of S(IV) species, sulfate ion is similarly important for sulfur mass balance and process optimization as well as being a major participant in calcium sulfate scale formation. The sulfate ion may be present in filtered slurry liquor or it may be present in the separated solids. The sulfate concentration range for the liquor was, by definition, set at 1-500 *mM* (See Table I). In the search for a suitable instrumental method, it was concluded that the automated laboratory techniques that were available at that time were not immediately acceptable without a critical review of the state of the art. Consequently, several candidate sulfate methods were evaluated including:

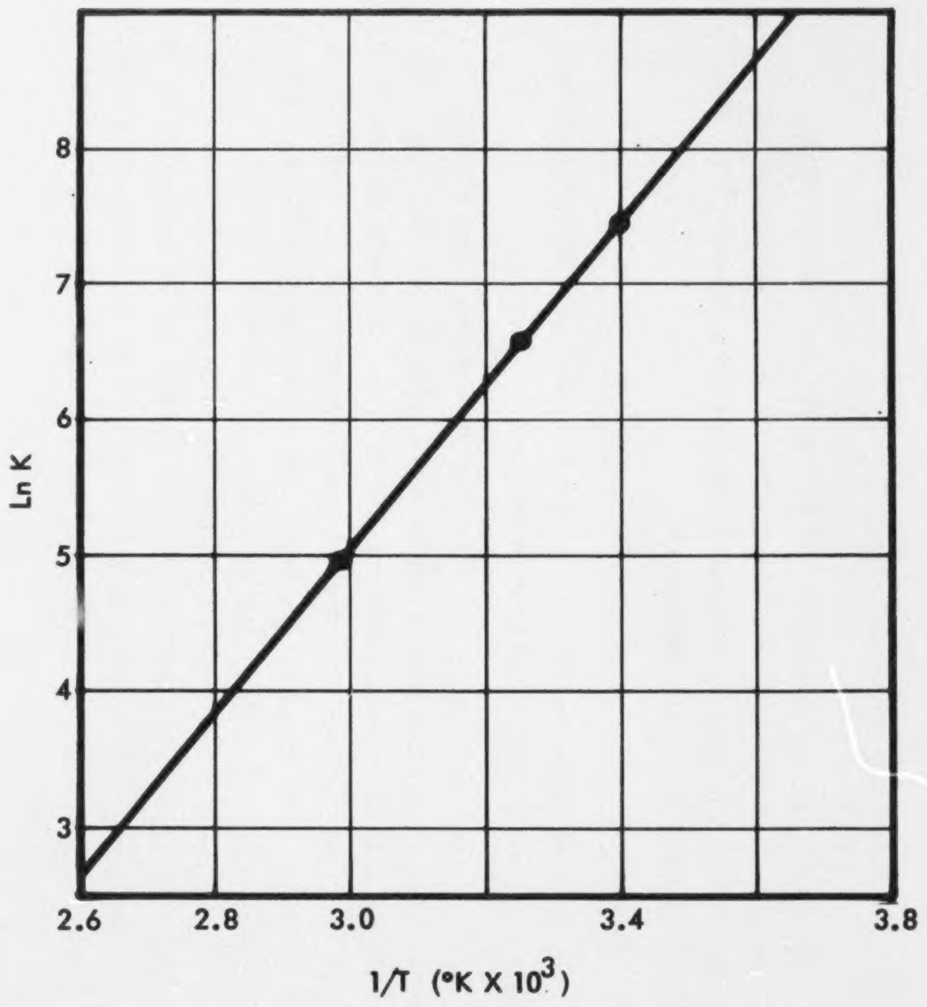


Figure 4. Change in Furfural Bisulfite Complex Equilibrium Constant with Temperature

- Titrimetric analysis
- Spectrophotometric analysis
    - Turbidimetric
    - Colorimetric
    - Atomic absorption
    - Infrared spectroscopy
    - Atomic emission
- Specific ion electrode

The results of our assessment of the technique, useful range, interferences, and relative ease of automation are presented below. This evaluation was used as the basis for selecting methods for limited feasibility testing in the laboratory.

2.6.1 Theoretical Evaluation of Sulfate Methods

The methods described below are for the most part indirect methods based on precipitation, usually with barium.

2.6.1.1 Titrimetric Methods - The titrimetric method involves the precipitation of sulfate with a barium salt with thorin, Sulfanazo, or other colorimetric or potentiometric end points. To avoid co-precipitation of carbonate and sulfite with barium, the analysis is conducted in acid solution. The range of the technique is 5-1000 mg sulfate/liter (0.05 to 10 *mM*) with a precision of 1-5%. Interference by nitrate, phosphate, chloride and cations is concluded to be either negligible or correctable. Automation of the titration technique can be accomplished in a batch analysis process using a potentiometric or colorimetric end point, however, the technique for acidifying and titration will require considerable development.

2.6.1.2 Turbidimetric Method - The turbidimetric method utilizing a photometer or turbidimeter is generally used in routine analysis of large volumes of samples where a precision of 5 to 10% is satisfactory. The sulfate concentration range applicable for this method is 0.1-1.0 *mM* with a minimum detection level of around 0.01 *mM* sulfate. Usually, barium chloride is used to precipitate the sulfate and interferences can be remedied. The time period between precipitation and turbidity reading is critical (up to 4 minutes with a maximum usually reached in 2 minutes).

In spite of the time lag for precipitation, and large dilution requirement, the fact that at least one automated instrument was marketed justified further consideration of the technique.

2.6.1.3 Barium Chloranilate Colorimetric Method - The indirect colorimetric determination of sulfate can be accomplished by using barium chloranilate to precipitate barium sulfate and release and equivalent amount of colored acid-chloranilate ion. Cations must be removed because of their interference, pH is critical (use pH 4.0), filtering and shaking are necessary and even at low concentrations the standard solutions may not obey Beer's Law. The long reaction times and required filtration times are also disadvantageous. The range of the method is from .02 - 4 *mM* sulfate. Calcium, ferric and aluminum ions completely precipitate the acid chloranilate ion and therefore must be removed by ion echange. Recent findings under Contract 68-02-0008 (Reference 1) have shown that chloride and nitrate concentrations present in the filtered slurry solution cause low results by more than 2%. Nonetheless, the method has been automated and deserves further consideration.

2.6.1.4 Benzidine Colorimetric Methods - Sulfate can be precipitated with benzidine hydrochloride and the excess can be measured by a variety of colorimetric methods:

- from generation of iodine
- reaction with furfural
- diazotization followed by coupling with phenol

Then in each case, the color complex is measured at the appropriate wave length.

2.6.1.5 Infrared Spectrophotometric - Quantitative IR analysis of solids for sulfate in calcined SO_2 reacted limestones has been reported by E. F. Rissmann and R. L. Larkin (Reference 8). The extrapolation of this technique to an automated method for dissolved sulfate ion in wet scrubber mother liquor appeared feasible.

2.6.1.6 Atomic Absorption Method (AA Method) - This technique is also based on precipitation of sulfate with a barium salt (chloride in this case), but measures the excess barium by atomic absorption spectroscopy. The useful range of this method is 0-1 *mM* sulfate with results comparable to volumetric and gravimetric measurements being reported. The AA method involves less operator handling than the volumetric method, but has a longer "start-to-finish" time because of long reaction time for equilibrium precipitation of barium sulfate under the established conditions. Modifications of the method reported by Dunk, et al (Reference 9) to reduce the solubility of barium sulfate at the working pH could result in decreased reaction time. The technique might be acceptable for laboratory application, however, it would not be a method of choice for on-line analysis.

2.6.1.7 - Specific Ion Electrode - Quantitative precipitation of sulfate is accomplished in a 50% dioxane 50% water solution using an excess of standard lead perchlorate. The excess lead ion may be quantitatively measured using a lead selective electrode. Activity of lead (measured by the electrode) must then be related to the concentration of lead by calculation using a knowledge of the total ionic strength. This technique has a dynamic range from fractions of a ppm to thousands of ppm lead. Excess lead is related directly to a sulfate concentration. The major drawbacks associated with the technique are high and variable ionic strength, the limited service life of cells, the large potential for interference and as with most of these methods the excessive elapsed time for complete precipitation with the resultant constraint on a continuous mode of operation.

2.6.1.8 - Sulfate By Difference from Total Sulfur - Recognizing the time limitation inherent in the precipitation methods and the time plus interference drawbacks of the chloranilate method, an alternative total sulfur technique was sought. It was believed that a combination of the furfural spectrophotometric method for S(IV) species coupled with a total sulfur technique could yield rapid and sufficiently accurate sulfate data to meet the process development criteria. In reviewing available direct instrumented methods it was found that a gap exists, ∿0.3 to 10 *mM* sulfur wherein sulfur cannot be determined.

As mentioned earlier, X-ray fluorescence provides a lower limit of approximately 10 *mM*, whereas a standard flame emission instrument, such as the Melpar FPD unit has a practical upper limit of approximately 0.3 *mM* (10 ppm). From theoretical considerations and work performed by other experimenters it appears possible to construct an instrument of the atomic emission (flame photometer) type for the analysis of total sulfur in a liquid stream that would fill the concentration range void.

In the region between 210 to 820*nM*, atomic sulfur has only one emission frequency, a sharp line at 216.9*nM*, respectively which would result from the combining of carbon and oxygen. High resolution spectrometers (∿0.1*nM*) which are available will reduce or eliminate the interference.

A total dissolved sulfur analyzer for the wet scrubber process stream should meet the following requirements:

- Capable of atomizing (vaporizing) a representative portion of the process stream on a continuous basis
- A hot zone, with optical windows, capable of disrupting all molecules
- Have sufficient spectroscopic resolution to reduce or eliminate all interferences
- For atomic absorption analysis have a light source that is capable of producing an emission at 216.9 *m*μ

The feasibility of this approach is based upon utilizing the 216.9 *m*μ atomic sulfur line which is from the excitation of non-ionized sulfur atoms. Recently, it has been demonstrated that sulfur can be measured quantitatively with both A.A. and A.E. techniques by utilizing microwave excitation (Reference 10). Spectrometrics Inc., Burlington, Massachusetts produce a unit that is similar to the type required for this determination, however, the instrument generates a plasma which would tend to ionize many or most of the sulfur atoms.

In the work of Syty and Dean (Reference 11) utilizing a fuel rich, air-hydrogen flame, they found a lower limit of detection of 15 μg/ml sulfur (∿0.5*mM*). They report a linear signal function with the square of concentration and a noiseless flame background. This technique is recommended for future development to augment RF and extend the detection limits to lower concentrations.

2.6.2 Experimental Screening of Candidate Sulfate Methods

Based on the findings above, a turbidimetric, an infrared and a titrimetric sulfate method were selected for experimental screening. To facilitate testing, the static scrubber slurry simulant described in Section 2.4.2

was utilized as the standard. The sulfate value of 5828 ppm was obtained gravimetrically, the referee method utilized as the standard for all comparisons.

2.6.2.1 Turbidimetric Method - Although the problems associated with turbidimetric sulfate analysis have previously been documented, the lack of more promising sulfate methodology dictated a brief investigation of this method. The method utilized is given in Reference 12. A calibration curve was constructed and the synthetic scrubber solution analyzed with the following results:

Method	SO_4^{2-} Concentration, ppm	% Deviation
Gravimetric	5828 (61 mM)	-
Turbidimetric	5460 (57 mM)	6.3

Not all possible interferants are present in the synthetic blend, however, the results indicate that a turbidimetric analysis may be the only alternative to an automated analysis considering the paucity of more promising methods. Experimentally the lower limit of detection (0.01 mM) is that previously reported while the upper limit can readily be adjusted through automatic dilution. The previously stated objections to this analysis are still valid but may possibly be circumvented and the method optimized to provide acceptable accuracy. In the single analysis above, the error of 6.3% is not acceptable in accordance with the allowable error of 5%, stipulated in Table I.

2.6.2.2 Infrared Spectrophotometric Method - The method of Rissman and Larkin (Reference 8) for the quantitative determination of sulfate in calcined SO_2 reacted limestone was investigated for its applicability to wet scrubber mother liquor. During this brief examination it was not possible to manufacture the 0.003 mm cells by vacuum deposition of metal which is a time consuming and costly procedure. Two experiments utilizing 0.015 mm path length cells with Irtran windows were conducted. In the first experiment, a sample of distilled water was run followed by the synthetic scrubber solution and then a 960 ppm sulfate reference standard. The results are as follows:

Solution	Absorbance	SO_4^{2-} Concentration
Reference	0.043	960 ppm (10 *mM*)
Synthetic Scrubber Solution	0.153	3420 ppm (36 *mM*)

A second experiment was conducted utilizing matched 0.015 mm cells blanking out the water absorbance in the reference beam. The results of the experiments were:

Solution	Absorbance	SO_4^{2-} Concentration
Reference	0.046	960 ppm (10 *mM*)
Synthetic Scrubber Solution	0.163	3400 ppm (35 *mM*)[a]

[a] Calculated

For these analytical conditions the deviations from the gravimetric values (5828 ppm) are greater than 40% error and hence the method is not recommended for further consideration.

2.6.2.3 High Frequency Titration Method - A high frequency titration for sulfate content of scrubber liquors was conducted using a Sargent Model V Oscillometer with $BaCl_2$ titrant. A sample of standard Na_2SO_4 and the synthetic scrubber solution were analyzed. The results of the titration were:

Solution	Experimental Results	Known Concentration	Deviation
Reference	957 ppm (10 *mM*)	960 ppm (10 *mM*)	-1.0%
Synthetic Scrubber Solution	6140 ppm (64 *mM*)	5828 ppm (61 *mM*)	+5.0%
Synthetic Scrubber Solution	5557 ppm (58 *mM*)	5828 ppm (61 *mM*)	-5.0%

The second scrubber sample was analyzed in 40% methanolic solution as opposed to aqueous solutions for the previous two runs. This method also demonstrates an apparent acceptable accuracy, however, the analysis time is considered excessive requiring on the order of 20 minutes for a single titration. This is because of equilibration time required between successive titrant additions. The use of mixed methanol solvent reduces the solubility of $BaSO_4$ and significantly shortens the equilibration times. It may also heighten interferences by other precipitating salts because the barium salts will become generally less soluble in the methanolic solution. The method has potential but will require development time and effort.

2.7 INSTRUMENTAL ANALYSIS OF CARBONATE

The required analysis range specified in Table I is 1-20 *mM* with an allowable error of 15%. Examination of the carbonate species distribution curves as a function of pH, presented in Figure 5, reveals that in a wet scrubber system operated in the range of pH 6.5 to 7.5, the bicarbonate species will predominate with moderate concentrations of carbonic acid.

Historically three analytical techniques have been utilized for the analysis of carbonate in aqueous solutions. The reactions involved are a) the acid-base equilibria between carbonate, bicarbonate and carbonic acid, b) the extremely low solubility of Ba, Ca and Sr carbonates and finally, c) the thermal removal of CO_2 from carbonic acid at low pH's. The relative merits of each of these with their appropriate end point detection devices are discussed in the following paragraphs.

2.7.1 Acid-Base Determinations

Titration of carbonates with either acid or base yields two end points corresponding to the following equilibria:

$$H_2CO_3 + H_2O = HCO_3^- + H_3O^+ \qquad K = 4.30 \times 10^{-7} \qquad (18)$$

$$HCO_3^- + H_2O = CO_3^{2-} + H_3O^+ \qquad K = 5.61 \times 10^{-11} \qquad (19)$$

Standard methods of end point detection would include conductometric, high frequency, thermometric, colorimetric (indicator) and potentiometric. All of these analysis end points would, however, be interfered with by HNO_2, H_2SO_3, HSO_3^- and HSO_4^-, metal ions and consequently, the methods are impractical.

2.7.2 Precipitation Reactions

The precipitation of Ca, Ba or Sr carbonates has been utilized for the gravimetric and turbidimetric analysis of carbonates. Representative solubilities are:

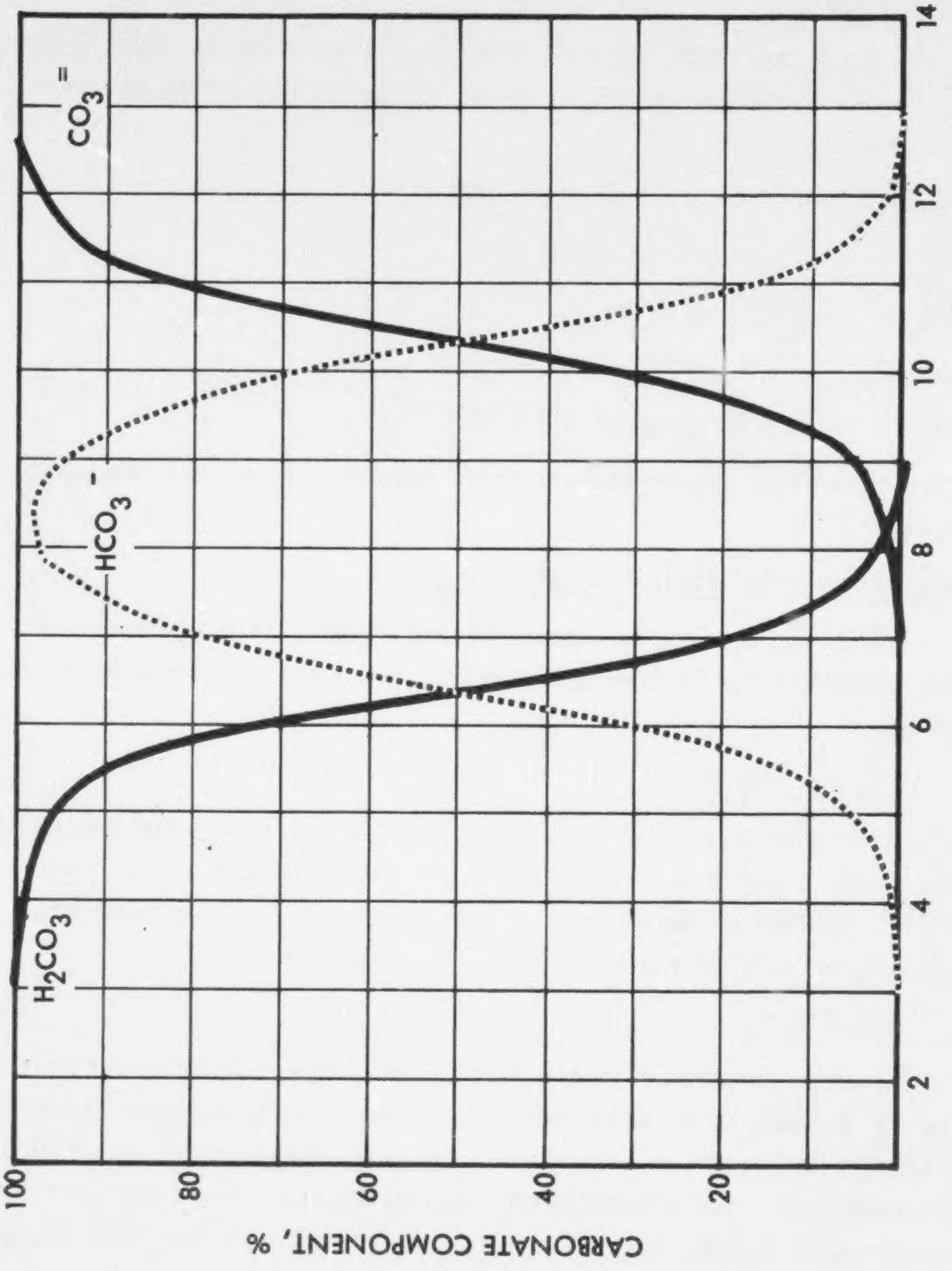


Figure 5. Carbonate Species as a Function of pH

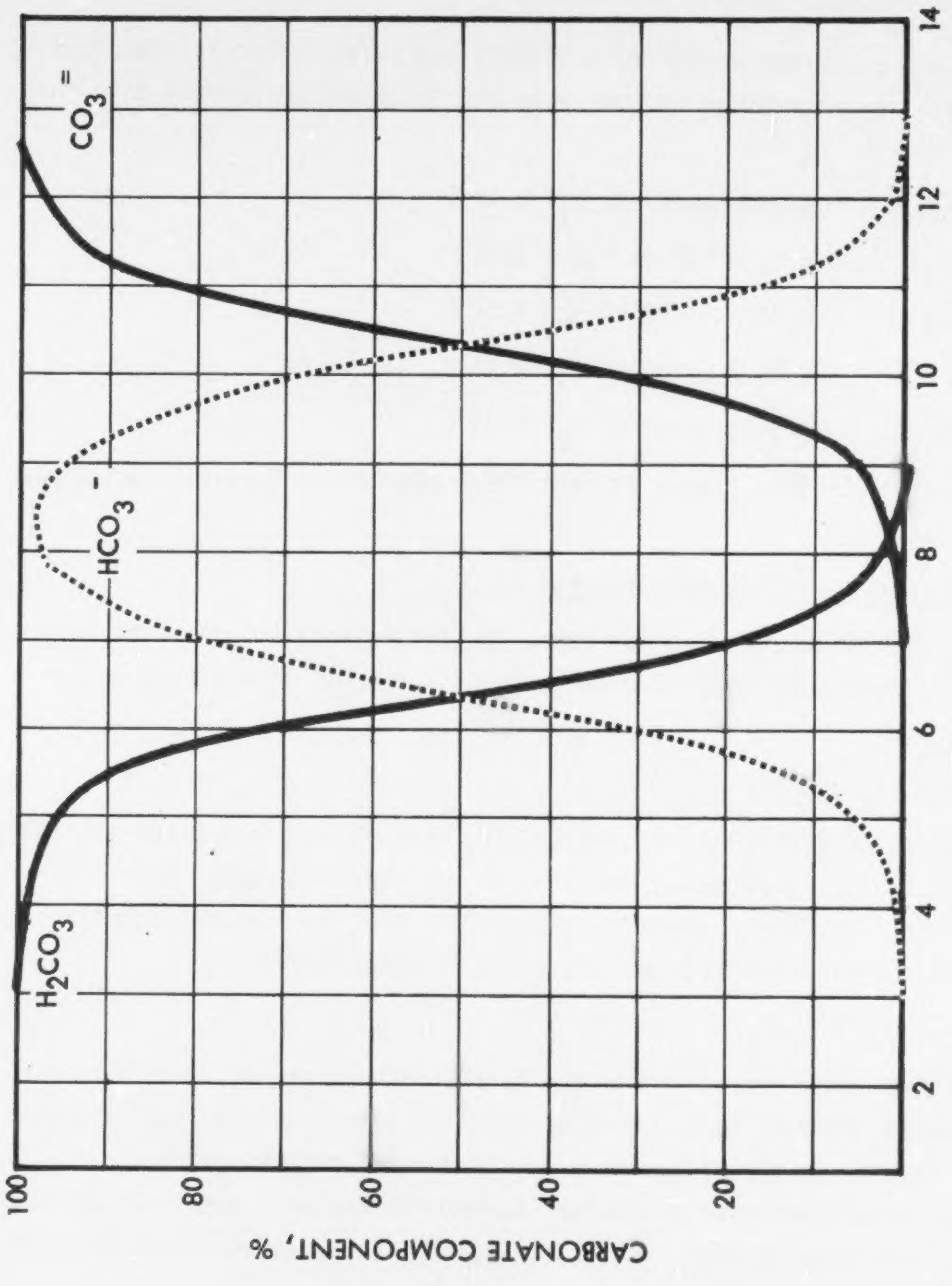


Figure 5. Carbonate Species as a Function of pH

$CaCO_3$ = 0.0015 g/100 ml H_2O @ 25°C

$BaCO_3$ = 0.002 g/100 ml H_2O @ 18°C

$SrCO_3$ = 0.0011 g/100 ml H_2O @ 18°C

In this case as in the preceding acid-base reactions, strongly interfering species will be present as evident from the following solubility data for scrubber sulfur species:

$CaSO_3 \cdot 2H_2O$ = 0.0043 g/100 ml H_2O @ 18°C

$BaSO_3$ = 0.02 g/100 ml H_2O @ 18°C

$BaSO_4$ = 0.0002 g/100 ml H_2O @ 18°C

$SrSO_3$ = 0.0033 g/100 ml H_2O @ 18°C

$SrSO_4$ = 0.0113 g/100 ml H_2O @ 18°C

Again these impurities appear to make these methods impractical for carbonate analysis.

2.7.3 Thermal or Acidimetric Removal of CO_2

The equilibrium between gas phase CO_2 and aqueous solution has been utilized extensively for carbonate analysis. The equilibrium may be represented by:

$$H_2O + CO_2 = H_2CO_3 \tag{20}$$

Many methods of estimating the evolved CO_2 include acidimetry and gas analysis. Gas analysis may be accomplished by gas chromatography, gravimetry (ascarite absorption) or manometric methods. For the scrubber solutions, potential interference from dissolved SO_2 is encountered.

$$SO_2 + H_2O = H_2SO_3 \tag{21}$$

However, the large difference in the first proton dissociation constants may allow CO_2 removal to be conducted specifically, while maintaining the sulfite species as bisulfite. The most promising methods which would eliminate the requirement for selective CO_2 removal however, are those utilizing specific detection systems such as non-dispersive infrared (NDIR) detection or, as a lesser candidate, gas chromatography.

The NDIR approach to simultaneous measurement of thermally liberated CO_2 and SO_2 is applied routinely to metals in a Laboratory Equipment Corp. thermal analyzer. The instrument output is displayed directly as % of C and % S in 60 seconds elapsed analysis time for both.

Given the ranging capability of NDIR, this detector should be readily adaptable to the ASTM acidimetric method for carbonate in lime (Method C25) which in turn can be used for scrubbing slurry.

Solids can be handled directly on the Leco Carbon-Sulfur Combustion Analyzer after separation and drying. This approach was demonstrated utilizing TRW's instrument (see Section 3.3 for discussion). Further evaluation and development of the thermal/acidimetric methods for CO_2 (and SO_2) are certainly warranted on the basis of the foregoing results.

2.8 SURVEY OF NITRITE/NITRATE INSTRUMENTAL ANALYSIS METHODOLOGY

Although methodology for nitrite/nitrate measurements in the wet scrubber liquor was not among the list of primary constituents under study, a preliminary review of methods was performed. The following brief listing of candidate methods and references is provided to assist current investigators and for consideration for future experimental evaluation and development. A comprehensive review of methodology for nitrogen-oxygen compounds is incorporated in the recently published monograph on analytical chemistry. (Reference 13).

2.8.1 Brucine Colorimetric Method

Several versions of the brucine colorimetric method for nitrite/nitrate determination are found in the literature. For total nitrite plus nitrate the EPA Federal Water Quality Office Method (Reference 14) is recommended for evaluation. The procedure is applicable for 0.1 to 2 ppm nitrate nitrogen (0.007 to 0.14 *mM* concentrations) and extreme care must be taken to control reaction conditions in order to obtain repeatable, accurate results. The degree of interference from scrubber constituents would have to be determined. The method reported by Fisher, et al, (Reference 15) allows for differentiation between nitrite and nitrate by varying acid concentration. FWQO recommends the brucine method as a manual technique, but it is potentially automatable.

2.8.2 Diazotization After Reduction

FWQO (Reference 14) recommends two automated nitrite/nitrate methods based on reduction with cadmium copper catalyst or hydrazine sulfate, reaction of NO_2 with sulfanilamide and coupling to an azo dye. Precisions for an interlaboratory evaluation are reported (+5.75, +18.10, +4.47 and -2.69% Bias). In testing saline water, standards containing 10 salt water constituents must be utilized.

2.8.3 Ion Specific Electrodes

Instrumental measurement of nitrate ion utilizing nitrate ion specific electrodes has been reported. In a flowing gas system designed by Dr. Martini (Reference 16), nitrogen oxides were reacted with ozone and the reaction products absorbed in a sodium nitrate aqueous solution. Measurement of nitrate concentration was achieved in a flow through liquid cell equipped with an Orion specific ion electrode. In a study funded by EPA under contract CPA 22-69-95 Driscoll, et al (Reference 17) found good correlation between results by the time consuming ASTM POS method and the nitrate ion specific electrode. Reduction of nitrate to ammonia and use of an ammonium ion specific electrode has been suggested as an improved approach to eliminate certain interferences.

3.0 TASK II - DEVELOPMENT OF PROCESS INSTRUMENTATION

The primary objective of this program was focused toward this task and was aimed at the identification of instrumental analytical methods suitable for on-line analysis of selected chemical species in the EPA Shawnee Power Plant wet limestone scrubbing process. The development of on-stream analysis methods will permit the rapid acquisition of data for the effective characterization of the process and timely elucidation of process parameter variations. High analytical accuracy (0.1% relative) is not a requisite of the needed methodology but rather the instrumental techniques must be reliable, reproducible, cost effective and the equipment easily maintained, and possess 2-5% relative accuracy.

On review of the scrubbing process variables several sampling requirements were identified relating to characterization of the scrubber mixture These sampling requirements are shown in Table XXI. During a literature review phase, sampling, separation and quenching of reactants were identified as major problem areas that had to be resolved prior to application of any analytical techniques to on-stream analysis. A system capable of handling a sampling rate of 30 samples per hour necessitated the use of a rapid separation of slurry and isolation of solid and liquid phases and was a key milestone prior to developing analytical techniques. The sampling rate was established assuming specific combinations of scrubber designs

TABLE XXI

LIMESTONE SLURRY SAMPLING REQUIREMENTS

- Slurry Solids Content - 0 to 15% w/w
- Slurry Sample Quantity - ≤1% of stream flow
- Instream Sampling Rate - <2X stream velocity
- Phase Separation
  - 100% removal of >0.5μ particles in liquid
  - Lag Time - <30 seconds
- Sampling Rate - 30 samples/hr, minimum
- Analysis Time - 2 min, max.
- Easily Maintained

and analysis location and sample frequency. An example which fulfills this requirement is three different scrubber design processes sampled every thirty minutes at five different locations. Variations of sampling locations up to eight and sampling frequency of up to fifteen minutes cover a wide range of samples to be analyzed. For the purpose of establishing the ability of an instrument to meet the continuous on-stream analysis requirements a total of 30 samples per hour was taken as a nominal value.

The effort to identify and develop suitable sampling and rapid slurry separation methodology involved vendor contacts, laboratory evaluation of prototype and standard equipment and testing of candidate equipment at vendor application laboratories. In order to assess the adequacy of a laboratory developed technique of analysis, it was necessary to produce a dynamic flue gas/scrubbing slurry sample. To accomplish this, a small scale laboratory scrubber test loop incorporating both a flooded bed and a Venturi type scrubber and a gas blending feed system was designed and constructed. Thus samples streams were generated which were simulations of the pseudo-equilibriated scrubber system, i.e., removal of a sample from the stream or change in operation would immediately be reflected in sample instability or dynamic change.

The following sections describe the activities associated with:

- The development of slurry sampling and separation techniques
- Extrapolation of X-ray methodology to continuous, on-line applications
- Design and plan for automation of the TRW furfural-bisulfite spectrophotometric method
- Operation and process variation capability of the laboratory bench scale wet scrubber process loop

3.1 SLURRY SAMPLING, SEPARATION AND QUENCHING

During the course of this task several vendors were contacted to determine whether they had equipment available which could separate a limestone/dolomite slurry meeting the following operating parameters:

- Flow rate —— to 300 lb/min (a portion of this flow could be diverted prior to the separator)
- Solids, % —— 0.5-15
- Particle size, micron —— 5-300
- Density of solids (unpulverized) g/ml —— 2.7-2.9
- Density of liquid, g/ml —— 1.005-1.080
- Temperature, °F —— to 150°F
- System to exclude air during and after separation —— both phases
- Time to effective separation —— 15 seconds

The directory of 48 separation equipment vendors and manufacturers compiled for this purpose is included as Appendix F. Of these ten companies replied positively that they had equipment which might fit these operating parameters. The separation principles identified included continuous discharge centrifuges, in-line filter cartridges, belt filters, and a continuous cyclone cone centrifuge.

Laboratory evaluation of these principles was undertaken using spent slurry obtained from the Key West Electric Company and equipment sold by deLaval, Sharples and Demco. A summary of the findings are shown in Table XXII. It was found that neither the cone centrifuge nor a combination of the solid bowl centrifuge-centrifugal cone provided clear-cut separation as indicated by slight cloudiness in the discharge fluids. An optically clear fluid would demonstrate excellent solids rejection and is needed for any subsequent colorimetric characterization of the liquid phase. However, inclusion of a polishing filter, such as an Acroflow in-line convoluted cartridge filter downstream resulted in a high capacity unit providing continuous transparent liquid for periods as long as several hours depending on the initial solid loading. A dual, parallel filter system from AFM-Caro was identified as a strong candidate for the downstream polishing filter component.

Several cartridge filter types including a wound cellulose fiber (Micro-Wynd), convoluted fiber screen (Cuno-Cal) and sintered metal screen (Micro-screen) with a variety of flow and particle retention properties are

TABLE XXII

SUMMARY OF LABORATORY EVALUATION OF SEPARATION METHODS

- Continuous centrifugation - deLaval Laboratory Gyro-tester
  Performance - 30 sec. operation at 0.5 gpm feed - 3% Zurn slurry
  Results - very nearly clogged
- Cone centrifuge (cyclone) - Demco 18mm cone
  Performance - continuous - pretreatment device
  Results - very promising
- Solid bowl centrifuge/cone-Sharples solid bowl/Demco
  Performance - minimum one hour continuous operation
  Results - slight turbidity
- Polishing filter - Acroflow in-line convoluted cartridge
  Performance - high capacity - quick interchange
  Results - optically clear output

available. The former two cartridges are low-cost and disposable while the metal screen is cleanable for reuse. A switching valve permits flow diversion from one filter housing to the second while a quick disconnect bolt allows rapid filter-cartridge removal and replacement.

3.1.1 Continuous Cyclone Separation/Filtration

The cyclone cone separator was fabricated by Demco as a prototype to meet TRW's design requirements and is shown schematically in Figure 6. The device consists of an 18-mm cone fabricated from 316 stainless steel and possesses an adjustable orifice control. The unit operates with a 35 psi minimum pressure differential with an inlet feed velocity of 46 ft/second and a minimum volume demand of 1 gpm. Throttling the underflow to cause an overflow to underflow ratio of 45, resulted in an overflow to underflow solids content ratio of 0.0204 with a 3% limestone slurry. Consequently, operation of the Demco in this mode permitted rejection of approximately 98% of the original solids content. The solution containing 2% of the original solids was readily handled through a continuous discharge centrifuge and polishing filters to provide optically clear liquid. It must be emphasized that the cyclone was operated at the minimum design pressure and flow because of slurry sample supply and pumping constraints within the laboratory. Much higher solids loading (to the 15% maximum) should be readily accommodated with equal or better solids separation at more optimum run conditions. That is, the efficiency of the cone can be improved at the Shawnee plant where up to ~6-10 gal/min of slurry can be diverted and pumped at higher pressure through the cyclone. The life time of the filters are at least one hour and use of the parallel bank system such as described above permits back flushing or cleaning to reactivate a spent filter when it is isolated from the flow loop. Low cost cartridges can be removed and discarded.

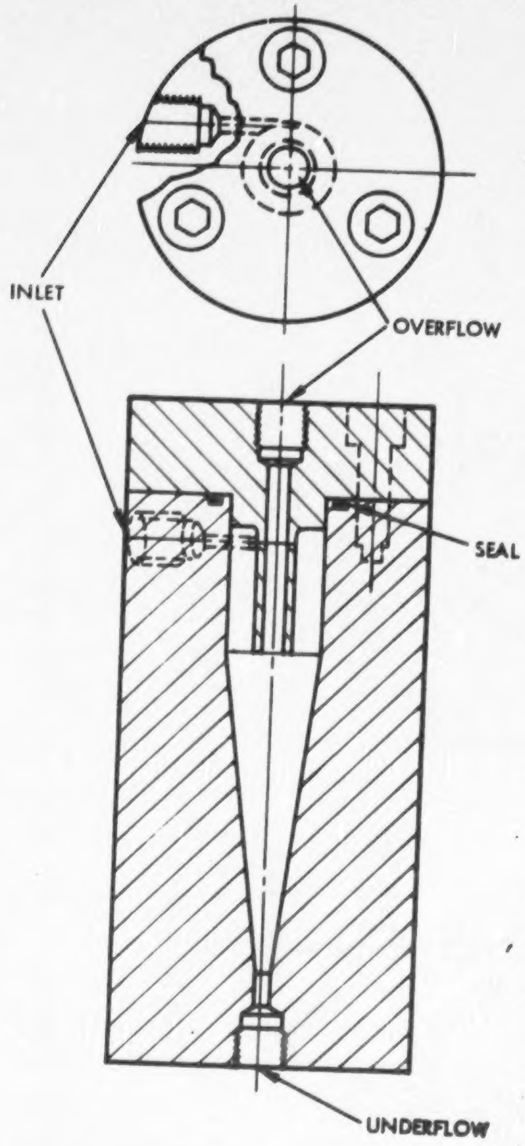


Figure 6. DEMCO Centrifugal Separator

The sampling and phase separation system shown schematically in Figure 7 is the recommended approach to permit continuous sampling for on-stream analysis. Two alternative systems (I and II) downstream of the cyclone are presented for consideration, however, the simpler and less costly of the two (Option I), is recommended for initial implementation and checkout.

Utilizing Option I, a clarification test was conducted on a 3% slurry made from the TVA high fly ash content limestone. The slurry was run through this laboratory scale clarification apparatus (cyclone, centrifuge and filter) for over 60 minutes, producing a clear, water white liquid on exit from the filter. All aspects of the test appeared normal and examination of the equipment post test revealed no anomalies. Option II

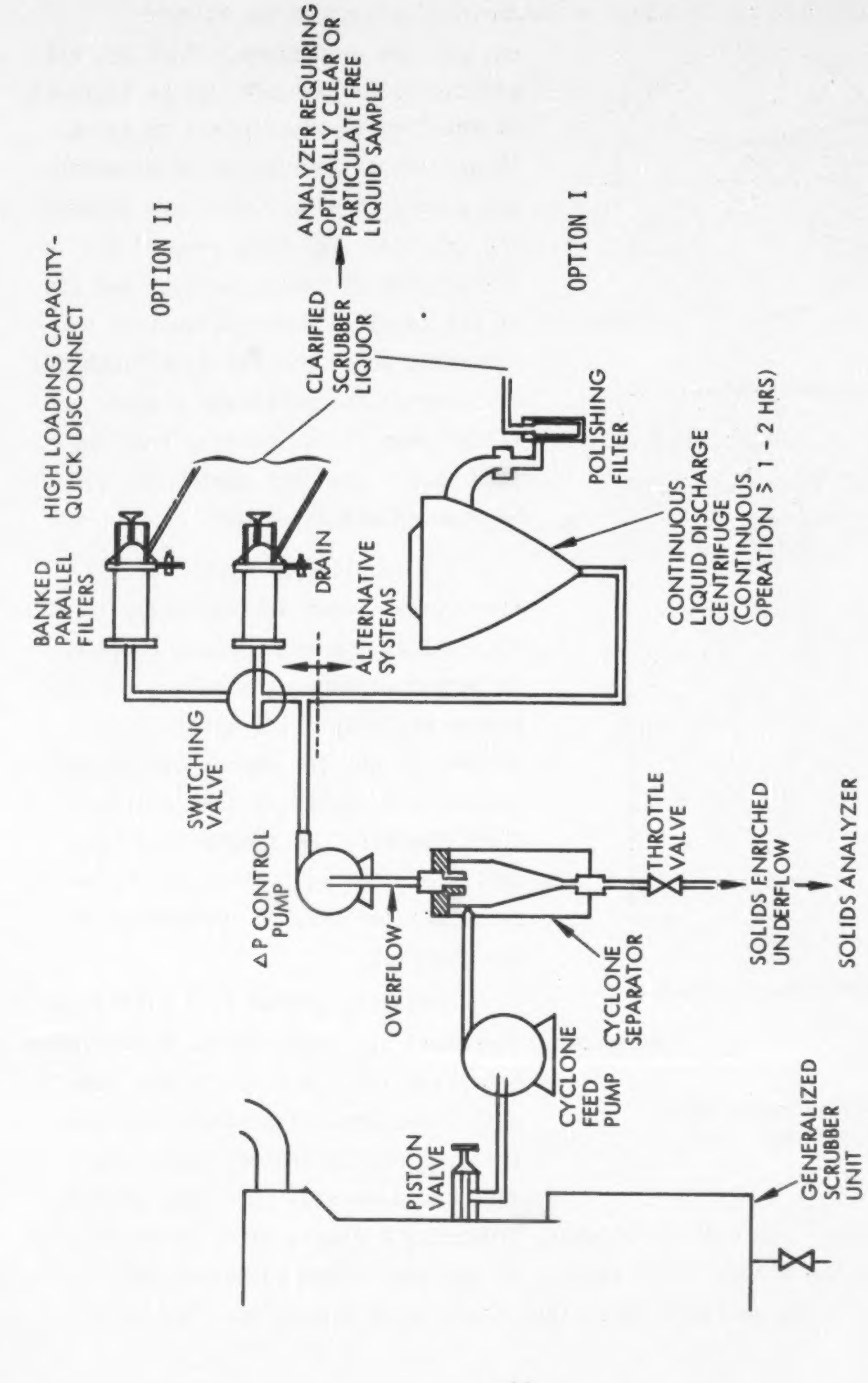

ANALYZER REQUIRING OPTICALLY CLEAR OR PARTICULATE FREE LIQUID SAMPLE
OPTION II
OPTION I
HIGH LOADING CAPACITY-QUICK DISCONNECT
CLARIFIED SCRUBBER LIQUOR
POLISHING FILTER
BANKED PARALLEL FILTERS
DRAIN
ALTERNATIVE SYSTEMS
CONTINUOUS LIQUID DISCHARGE CENTRIFUGE (CONTINUOUS OPERATION ≥ 1 - 2 HRS)
SWITCHING VALVE
ΔP CONTROL PUMP
OVERFLOW
THROTTLE VALVE
SOLIDS ENRICHED UNDERFLOW
SOLIDS ANALYZER
CYCLONE SEPARATOR
CYCLONE FEED PUMP
PISTON VALVE
GENERALIZED SCRUBBER UNIT

Figure 7. Schematic of Continuous Slurry Separation Approaches

could not be fully evaluated for operation time because the dual filter system was not available, but nonetheless it is expected to be very nearly as cost effective on an operation basis by optimizing the cyclone operation and utilizing re-usable filters.

Because of the concern that mass transfer between solid and liquid phases in a non-equilibrium slurry might cause a problem (when separating by the Demco cone-polishing filter technique because of filter cake build-up), a worst case plan was implemented to determine the effect of filter cake build-up using a batch filtration method.

The experiment permitted comparison of the chemical composition of filtrates taken from consecutive filtrations through an increasing filter cake size and fresh filtrations. The experiment consisted of taking 200-ml aliquots from a highly agitated slurry (3% w/v solids) and filtering through a millipore filter in a deaerated environment. After a period of time the slurry was sampled again and an additional 200-ml aliquot was taken and placed in the filter already containing the filter cake from the previous filtration. A comparison aliquot was taken at the same time and was filtered through a clean filter. The time of filtration was governed by the time required to pass the filter containing the consecutive runs; the rate of filtration through the fresh filter was regulated by the downstream pressure. This operation was repeated two additional periods to provide a total of four sequential sets of aliquots. The filtrates were retained in deaerated environments and analyzed for bisulfite and calcium contents and for pH measurement. Details of the experimental procedure are presented below and the results are presented in Table XXIII.

> To 4360 ml of boiled, argon sparged deionized water were added 90 g limestone, 5.17 g $NaHSO_3$ and 45 g of fly ash (metals added, which had been neutralized with HCl* and then washed in

---

*Because of insufficient TVA fly ash to conduct these experiments, fly ash obtained from the Nevada Power Plant, Moapa, Nevada was used. The chemical composition of the Moapa fly ash is different than that of the TVA fly ash and consequently, metals were added to provide comparable metallic constituents to that expected from the TVA fly ash. In addition, the fly ash was considerably more basic, consequently, the fly ash was neutralized prior to use.

TABLE XXIII

EFFECT OF FILTER CAKE BUILDUP ON SIMULATED WET SCRUBBER FILTRATE COMPOSITION

Filtering Type		Slurry Mixing Period, Min. 5	45	75	140
Consecutive Filtration					
Filtering Variables	Time, min	15	21	60	50
	Filter Cake, g/in^2	4	8	12	16
Filtrate Composition	pH	7.2	7.2	8.0	7.8
	Bisulfite, *mM*	5.65	3.46	2.99	2.60
	Calcium, *mM*	2.43	1.05	0.70	0.55
Fresh Filtration					
Filtering Variables	Time, min	15	18	60	50
	Filter Cake, g/in^2	4	4	4	4
Filtrate Composition	pH	7.2	7.6	7.8	8.0
	Bisulfite, *mM*	5.65	3.41	3.21	[illegible].71
	Calcium, *mM*	2.30	1.12	0.80	0.62

deionized water). This yielded a synthetic scrubber solution with 3% solids and 12 *mM* bisulfite. This slurry was placed in a magnetic stirrer in a GN_2 purged dry bag. Also present in the dry bag were two glass millipore filtering sets with 10μ Teflon filters and 1.5-in^2 of filter area.

The results show good comparison between the consecutive single batch filtration filtrate composition indicating little contribution of liquid-solid mass transfer to the key liquid phase chemical constitutents. It is interesting to note that the bisulfite and calcium ion concentrations decrease as a function of elapsed time of slurry mixing which, as will be discussed later in Section 3.4, is attributed to the kinetics of calcium sulfite precipitation. Because the elapsed time of separation anticipated when the Demco cone-polishing filter are used will be considerably less than that experienced during these experiments, it is believed the findings here will be valid until comparable filter cake buildup (approximately 0.5-inch) is observed. It is recommended however, that similar experiments be conducted using the full scale Demco (1 gal/min) flow on the TVA process units to confirm the results of our findings prior to using the apparatus in the field.

3.1.2 Solids Discharging Methods

A continuous staged separation concept was devised which is capable of achieving "instantaneous quenching of reaction" within an arbitrary allotted time of 15 seconds in such a manner as to present a "dry" stream of slurry solids for continuous analysis. In one conceptual design shown in Figure 8, the slurry feed may be taken from the slurry stream and fed to a solids discharging centrifuge. In this system the process stream at the point under scrutiny is split and the sample stream enters a liquid/liquid/solid separator. A second heavy liquid phase such as a Freon, trichlorethylene or other heavy inert solvent would be added to the slurry as it entered the separator. Because of the toxic nature of many of the candidate solvents, appropriate containment of the vapors during handling and evolution is required via forced air hoods or vents. As shown in the schematic drawing, the light, clear aqueous phase is separated from an annular zone near the center, the denser non-aqueous phase is ejected from an intermediate zone while the solids, essentially free from aqueous liquid contamination are continuously discharged from the outermost zone and transferred to the quartz filter carrier belt.

Whereas the liquid/liquid/solid type centrifuge with its inert solvent wash potential capability was not demonstrated, a Sharples Super-D Canter P-600 was tested at the Pennwalt Corporation application laboratory. A 20-gallon aliquot of Zurn spent slurry containing 3.86% solids was processed at ambient temperature, various feed rates and two bowl speeds. The following experimental data were obtained and are presented graphically in Figure 9.

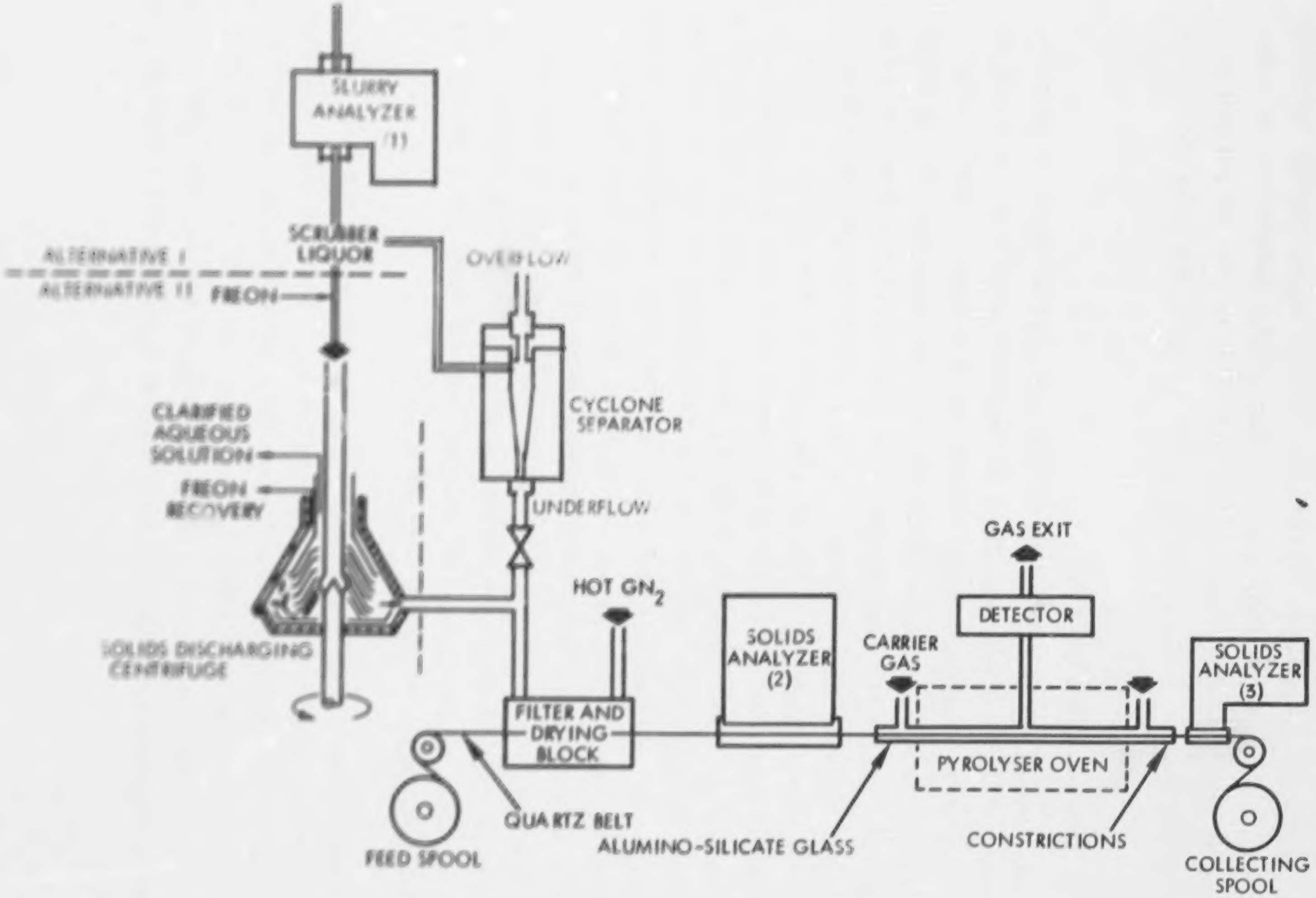

SLURRY
ANALYZER
(1)
SCRUBBER
LIQUOR
ALTERNATIVE I
ALTERNATIVE II
FREON
OVERFLOW
CYCLONE
SEPARATOR
UNDERFLOW
CLARIFIED
AQUEOUS
SOLUTION
FREON
RECOVERY
SOLIDS DISCHARGING
CENTRIFUGE
HOT GN2
FILTER AND
DRYING
BLOCK
QUARTZ BELT
FEED SPOOL
SOLIDS
ANALYZER
(2)
ALUMINO-SILICATE GLASS
CARRIER
GAS
GAS EXIT
DETECTOR
PYROLYSER OVEN
CONSTRICTIONS
SOLIDS
ANALYZER
(3)
COLLECTING
SPOOL

Figure 8. Schematic Design of Continuous Solid Separation and Analysis Apparatus Concept

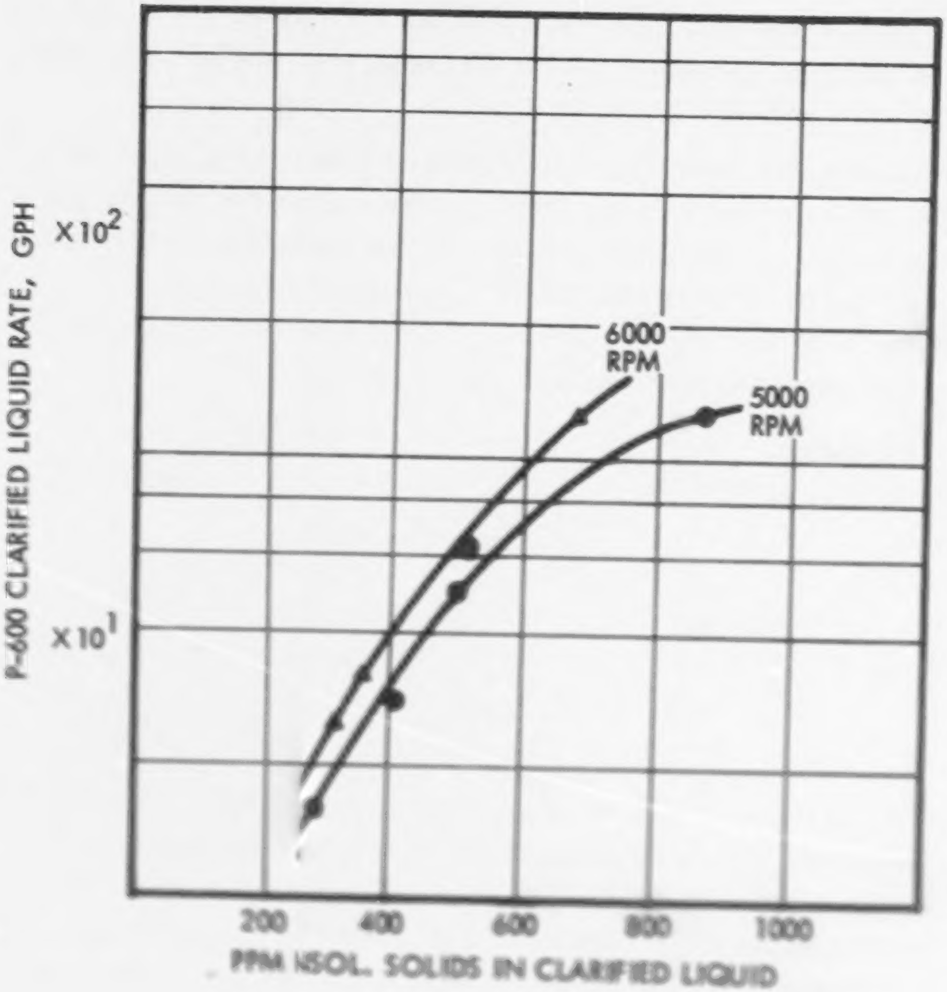


Figure 9. Flow Rate vs Clarity for Sharples Super-D Canter

Test No.	1	2	3	4	5	6	7	8	9	10
Clarified Liquid										
rate, gph	50	16	28	63	126	25	63	32	95	126
insol. solids, ppm	500	290	410	520	870	320	530	360	600	680
Mechanical Conditions										
bowl speed, rpm	5000					6000				
conv. diff., rpm	50					60				
pond	3					3				

The feed slurry contained 3.86 % w/w (38,600 ppm) insoluble solids. The composite solids sample collected during the test program contained 20.0 % w/w moisture.

Thus it can be seen that the P-600 provides a clarified liquid that can be fed to a polishing filter and solids discharge with ~20% moisture amenable to the solid analysis system in Figure 9.

Alternatively, the centrifuge unit (which is a major cost item) may be omitted and the underflow from the DEMCO cyclone used as the feed to the moving belt filter. In addition to concentrating the solids in the underflow, classification of size distribution also occurs. For the 3% w/w solids loaded Zurn spent slurry, the size distribution in a microscopic examination of under and overflow gave the following:

Overflow

Size, μ	Cum % No.
<10	87
<20	99
<30	100

Underflow

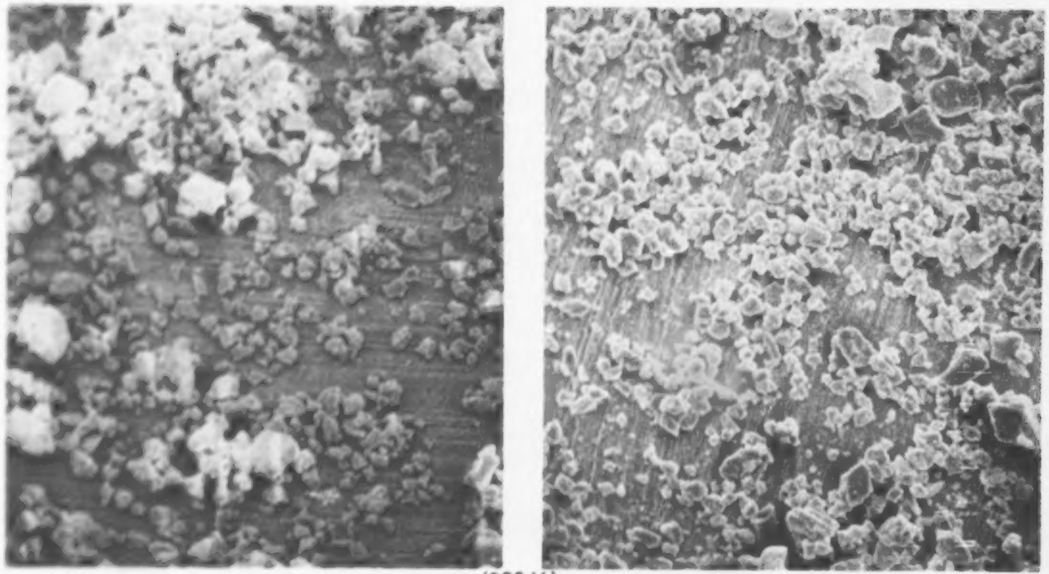
Size, μ	Cum % No.
<10	53
<20	88
<30	96
<40	98
<50	99.5
<60	100

This obvious classification is a variable dependent on cyclone efficiency parameters. Figure 10 shows photomicrographs of the particles isolated from the overflow and underflow. Qualitative XRF analysis of the solids from the separation indicated no significant classification by species or elements. With a 98% w/w concentration of solids in the underflow, some differentiation by compounds will be tolerable.

OPERATING SPECIFICATIONS:

INLET FEED, FPS	46
VOLUME DEMAND, GPM	1
PRESSURE, PSID	35

SEPARATION CAPABILITY 97% OF PARTICLES LARGER THAN 4.3 MICRONS WITH SPECIFIC GRAVITY OF 2.3



(300 X)

3 TO 10 MICRONS

TEST RESULTS:	UNDERFLOW	OVERFLOW
PARTICLE SIZE <10 μ	53%	87%
FRACTION OF SOLIDS	0.524	0.476
FRACTION OF VOLUME FLOW	0.022	0.978
XRD CHEMICAL ANALYSIS (SIGNIFICANT DIFFERENCES)	Ti, Fe, Br, Cl, K, S, Sr	Ti ABSENT, Fe, Br, Cl, K INCREASED S, Sr SAME

Figure 10. Zurn Slurry Separation by Demco Cone

Relative and approximations for the three slurry separation subsystems exclusive of the moving belt filter for solids transport but inclusive of the dual polishing filters and pumps described above are as follows:

DEMCO Cyclone	∿$600
Solid Bowl (Liquid Discharging Only)	∿$3,000
Liquid/Liquid/Solid Discharging	∿$15,000
Super-D-Canter	∿$10,000

In the filter/drying housing which is the second stage residual inert solvent or remaining moisture is volatilized in heated high pressure dry nitrogen stream before the solids pass into the solid analyzer sections.

3.2 CONTINUOUS ON-LINE X-RAY FLUORESCENCE (XRF) METHODOLOGY

As described in Section 2.4.1 the XRF technique was judged the best candidate instrumental technique for laboratory and continuous, on-line analysis for elements and cations in the composite slurry, the separated solids and for dissolved species in the liquor (sensitivity permitting). Limiting the evaluation and development effort to those candidate instruments that could conceivably provide the on-line technology, three units are evaluated and ranked in Appendix D, i.e., 1) ARL, 2) G.E. and 3) Kevex. Timely experimental evaluation utilizing the standard specimens delineated in Table VIII was possible only at the ARL and Kevex laboratories. Details of the experimental activity related to the ARL unit that were pertinent to the conclusions presented in Appendix D are discussed below while the Kevex data is highlighted in the appendix.

A trip was made to Applied Research Laboratories (Sunland, California) for the purpose of evaluating their process control X-ray quantometer (PCXQ) for on-line analysis of selected chemical species in the Shawnee plant limestone wet scrubbing process. The 14 specimens listed in Table VIII were run on ARL's laboratory X-ray Quantometer 72000. Although the Model 72000 accommodates only dry specimens, ARL personnel assured us that it is the same basic X-ray fluorescent spectrometer instrument as the Model PCXQ minus slurry presenter modifications.

Several PCXQ units with slurry presenter modifications in beginning stages of fabrication and assembly were examined. Up to 15 slurry streams can be analyzed sequentially in an automated mode for elements from magnesium upwards in the periodic table with the PCXQ. In addition, an override can be placed on the automated mode and batch solid samples may be analyzed by shutting off the appropriate slurry feed streams. Nine spectroscopic channels of information are available and nine elements in each of the 15 slurry streams can be simultaneously detected and analyzed. A pulp density monitor is incorporated into the system along with a fixed external standard. Flow rates through the slurry sample cell can be 5, 15 or 50 liters/minute.

The data generated on the ARL-PCXQ are in the form of voltage ratios and are denoted

$$I_s/I_{ES}$$

where: I_s = voltage output from sample

I_{ES} = voltage output from a fixed external ARL standard

The signal data are presented in Table XXIV. An analysis of these data and curves generated from them lead to the observations and conclusions presented below.

3.2.1 Limit of Detection

The limit of detection for sulfur is 0.03% absolute* in $CaCO_3$ and limestone-base specimens on the ARL-72000 unit. An on-line slurry unit PCXQ utilizing a helium X-ray path and a Kapton cell window will have a poor limit of detection. The limit of detection is significantly less than the 0.25% absolute value which has been discussed as the lowest reasonable value which is likely to be encountered for the slurry but higher than the lowest 1 mV for the liquid phase (0.03% is equivalent to 9.4 mV). For the other elements of concern, e.g., Ca, Mg, Fe, Cl, etc., the limit of detection is much lower than the 0.1% tentative requirement (Appendix D).

3.2.2 Repeatability

The repeatability of the 72000 unit was demonstrated to be more than adequate for projected use. The precision of the slurry model should be close to the same because the precision is largely controlled by both the X-ray spectrometer design and signal processing technique both of which are

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*Conditions: vacuum, 0.25-mil thick polyethylene window, 2-minute count

TABLE XXIV
SIGNAL DATA FROM ARL QUANTOMETER 72000

SAMPLE	Mg	Al	S	Fe	Ca[a]
001 $CaCO_3$ (reagent grade)	0.220	0.010	0.054	0.344	10.448
Rerun 2 days later	0.210	0.010	0.054	0.360	0.524
002 $CaCO_3$ + 7.9% $CaSO_4$ (1.85% Sulfur)	0.220	0.018	1.294	0.416	9.653
Rerun 2 days later	0.212	0.019	1.332	0.422	7.873
003 $CaCO_3$ + 14.6% $CaSO_4$ (3.44% Sulfur)	0.206	0.007	2.697	0.360	9.068
Rerun 2 days later	0.198	0.008	2.666	0.390	7.412
004 TVA Limestone (0.05% Sulfur)	2.881	0.167	0.074	1.276	9.933
005 Limestone + 7.9% $CaSO_4$ (1.87% Sulfur)	2.655	0.140	2.031	1.166	9.352
005 (Repeat) Limestone + 7.9% $CaSO_4$ (1.87% Sulfur)	2.630	0.140	2.052	1.169	9.354
005 With 0.25 mil Kapton	0.306	0.036	1.000	1.182	8.512
004 (Repeat)	2.879	0.168	0.076	1.279	9.928
004 With 0.25 mil Kapton	0.285	0.041	0.059	1.294	9.037
006 Limestone + 14.6% $CaSO_4$ (3.44% Sulfur)	2.330	0.134	4.544	1.127	8.799

(a) Sensitivity changes were made in calcium determinations so the numbers obtained two days apart for calcium will be different.

TABLE XXIV (CONTINUED)

SAMPLE	Mg	Al	S	Fe	Ca
007 $CaCO_3$ + 7.9% $CaSO_4$ +1% Fe (1.81% Sulfur)	0.211	0.008	1.408	6.082	9.592
008 Limestone-TVA FA	4.806	6.275	1.023	4.000	2.576
009 Limestone-Zurn FA	2.026	0.082	0.149	1.877	9.850
010 1.5% TVA FA in 98.5% Epoxy	0.307	0.313	0.096	8.710	0.133
011 10% TVA FA in 90% Epoxy	0.786	1.976	0.298	4.000	0.866
012 1.5% Zurn FA in 98.5% Epoxy	0.299	0.060	0.068	2.160	0.362
013 10% Zurn FA in 90% Epoxy	0.344	0.062	0.072	2.180	2.376
014 $CaCO_3$ + 7.2% $CaSO_4$ + 7.2% Na_2SO_3 (-40 Mesh) (3.43% Sulfur)	0.192	0.008	1.310	0.361	9.612
New Run	0.194	0.008	1.385	0.426	7.786
New Sample	0.197	0.008	1.439	0.380	7.662
Na_2SO_3 (reagent grade)	0.088	0.005	6.649	0.585	0.031
Na_2SO_4 (reagent grade)	0.100	0.005	5.832	0.700	0.031
NaCl (reagent grade)	0.249	0.915	0.077	0.493	0.030
NaCl with 0.25 mil Kapton	0.125	0.200	0.054	0.528	0.029
ARL (Reagent Grade) $CaCO_3$	0.272 0.266	0.033 0.032	0.106 0.092	0.490 0.505	8.382 8.398
003 With 0.25 mil Kapton	0.147	0.007	1.351	0.424	6.670

the same in the PCXQ and 72000 systems. The repeatability of a single measurement was checked by determining the sulfur content in sample 002 eleven times. The sample contains 1.85% S and the mean voltage ratio was 1.397 ± 0.0054 where the uncertainty is the standard deviation. The percent standard deviation is 0.4%, far less than the 3% which has been viewed as a requirement.

System repeatability after a period of time, is good as shown from an experiment in which the same samples were analyzed two days later. The findings presented in Table XXV shows that the two sets of data always agree to within 10% of their nominal value and more frequently agree to within 4%. Again, the conclusion is that a 10% fluctuation around a nominal 1% sulfur value will be readily detected.

TABLE XXV

ARL-72000 VACUUM QUANTOMETER REPEATABILITY DATA

Specimen and Element	Voltage Ratios		Relative Reliability %
	First Data Set	Second Data Set 2 Days Later	
Sample 001			
Mg	0.220	0.210	5
S	0.054	0.054	0
Fe	0.344	0.360	3
Sample 002			
Mg	0.212	0.220	4
S	1.294	1.332	3
Fe	0.416	0.422	2
Sample 003			
Mg	0.206	0.198	4
S	2.697	2.666	3
Fe	0.360	0.390	8

3.2.3 Matrix Effects

Figures 11 and 12 demonstrate that both elemental sulfur and calcium working curves are influenced by the matrix material in which the sulfur

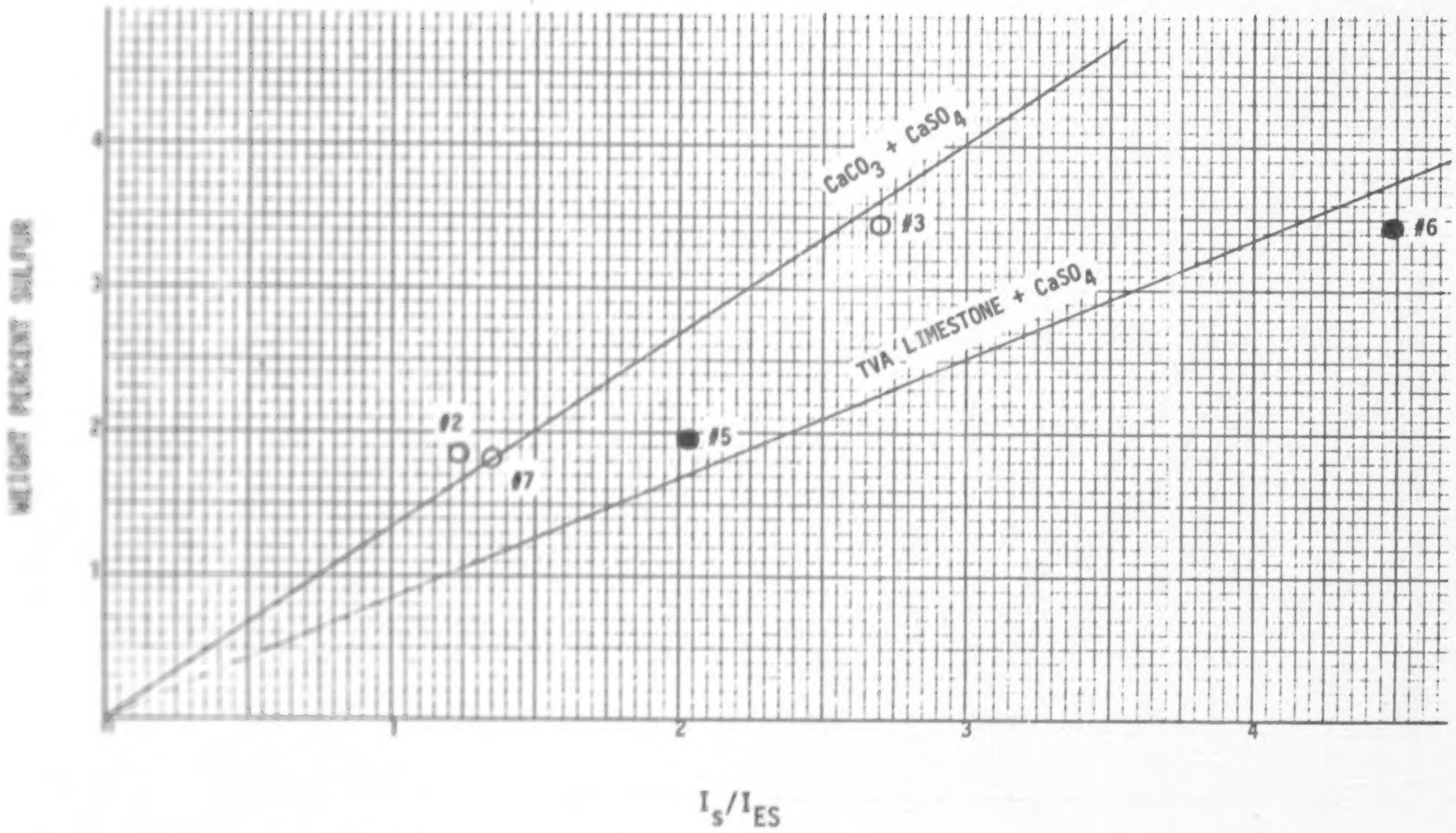

Figure 11. Working Curves for Sulfur Analysis

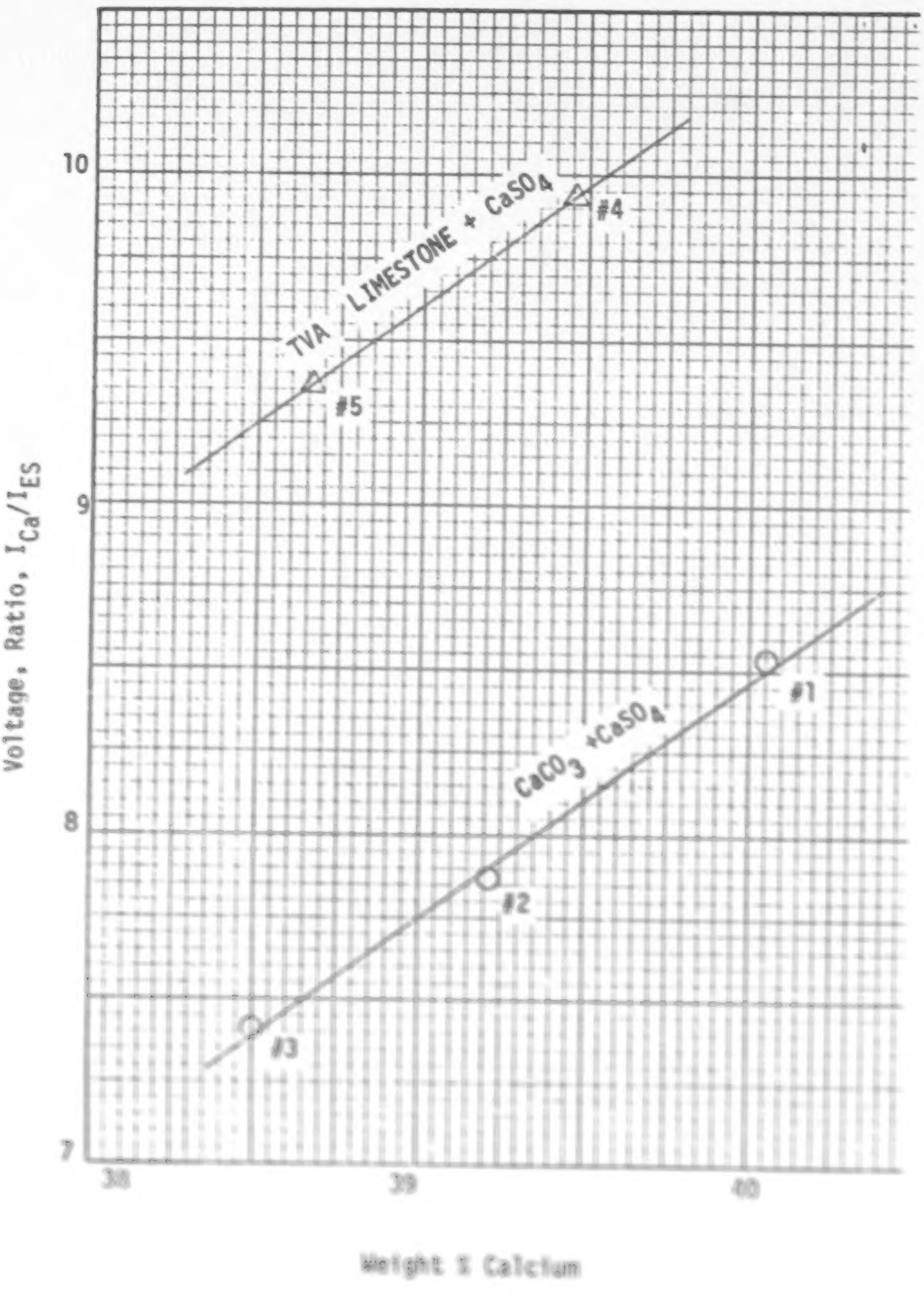

Figure 12. Calcium Working Curves

is contained. In Figure 11, two curves were generated for specimens with the same sulfur contents; the only difference in the specimens is that one set contained limestone (natural $CaCO_3$) as a diluent for $CaSO_4$ and one set contained reagent grade $CaCO_3$. Particle sizes were about the same. It is clear from the figures that the output ratio from the Quantometer is influenced by the matrix, and that separate working curves are needed for $CaCO_3$ and limestone matrices. The explanation for this effect may rest in the presence of trace elements in limestone and it may very well be possible to take this effect into account by monitoring the magnesium content on a separate spectrometer.

3.2.4 Quantitative Interpretation

Using the limestone + $CaSO_4$ working curves in Figures 11 and 12, the following information was determined for the limestone/TVA flyash and limestone/Zurn flyash specimens:

- For quantitative analysis it is essential to prepare reference specimens having all the same ingredients including limestone and flyash. In the studies reported here poor agreement with wet analysis was obtained using working curves which did not include flyash. However, in previous work conducted at TRW, excellent agreement was obtained on the TVA specimens when flyash was added to the matrix.

- The TVA specimen appears to be considerably different than the Zurn flyash specimen with regards to other elements also. The TVA flyash specimen contains approximately 2-1/2 times the quantity of Mg, 75 times the quantity of aluminum, twice as much Fe, and 1/4 as much Ca as the Zurn flyash specimen. Specimen 007 contained 0.9 % w/w Fe to check interference between iron and sulfur in a $CaCO_3$-base sample. The curve in Figure 11 (points #2 and #7) indicates that the 0.9 % w/w iron had virtually no effect on the 1.8 % w/w sulfur determination.

3.2.5 Particle Size Effects

The output signal is influenced by particle size in the specimen. This effect was dramatically illustrated by samples 006 and 014. Both specimens contain 3.44 % w/w sulfur except 014 contains about half the sulfur as the sulfite ion. At first, it was found that the signal from

014 was about half of what was expected and it was thought that a distinction might be made between the $SO_4^=$ and $SO_3^=$ ions. Auxiliary determinations on reagent grade Na_2SO_4 and Na_2SO_3 proved that such a distinction was not possible, and instead it was observed that a large difference existed between the particle sizes of $CaSO_4$ and Na_2SO_3. An additional sample was prepared in which all the constituents were passed through a 400 mesh screen (37 micron opening). The data for this sample showed that as long as the particle size remains small (<37 micron), spurious results due to particle size will be eliminated. The particle size effect should be common to all X-ray fluorescence units and is not unique to one vendor. No problem is anticipated in actual wet scrubber operation where over 80% of all particles are smaller than 30 microns (This observation was made from classification of spent limestone slurry solids from Zurn, KPL and Shawnee wet limestone facilities).

3.2.6 Dilution Effects

Dilution effects (or, stated another way, the effects of solids loading) are handled in a straightforward manner by use of a concentration-loading-signal map. Figure 13 contains experimental data in a hypothetical map. The main point is that the signal strength is proportional to the solid loading fraction for the TVA flyash. Secondly, the broken lines indicate the manner in which such a map might be used in a real operation. A signal strength value for sulfur is first determined. A percent solids loading is next determined *via* a pulp density gauge which is built into the ARL system. The point where the two lines intersect gives the weight percent sulfur in the solid portion of the slurry sample.

3.2.7 Analysis of Liquid Samples

Throughout the evaluation session it was realized that the ARL-72000 was a highly optimized laboratory unit and that a lower level of performance would be expected in the PCXQ slurry system. As a result, the following series of experiments was conducted to determine, in an appropriate manner, the behavior which might be expected on a PCXQ system.

The experiments consisted simply of covering the dry samples with a 0.25-mil sheet of Kapton*. The voltage ratios were compared with those obtained with Kapton absent. The data are presented in Table XXVI. For

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*Kapton is the slurry cell window material in the PCXQ system.

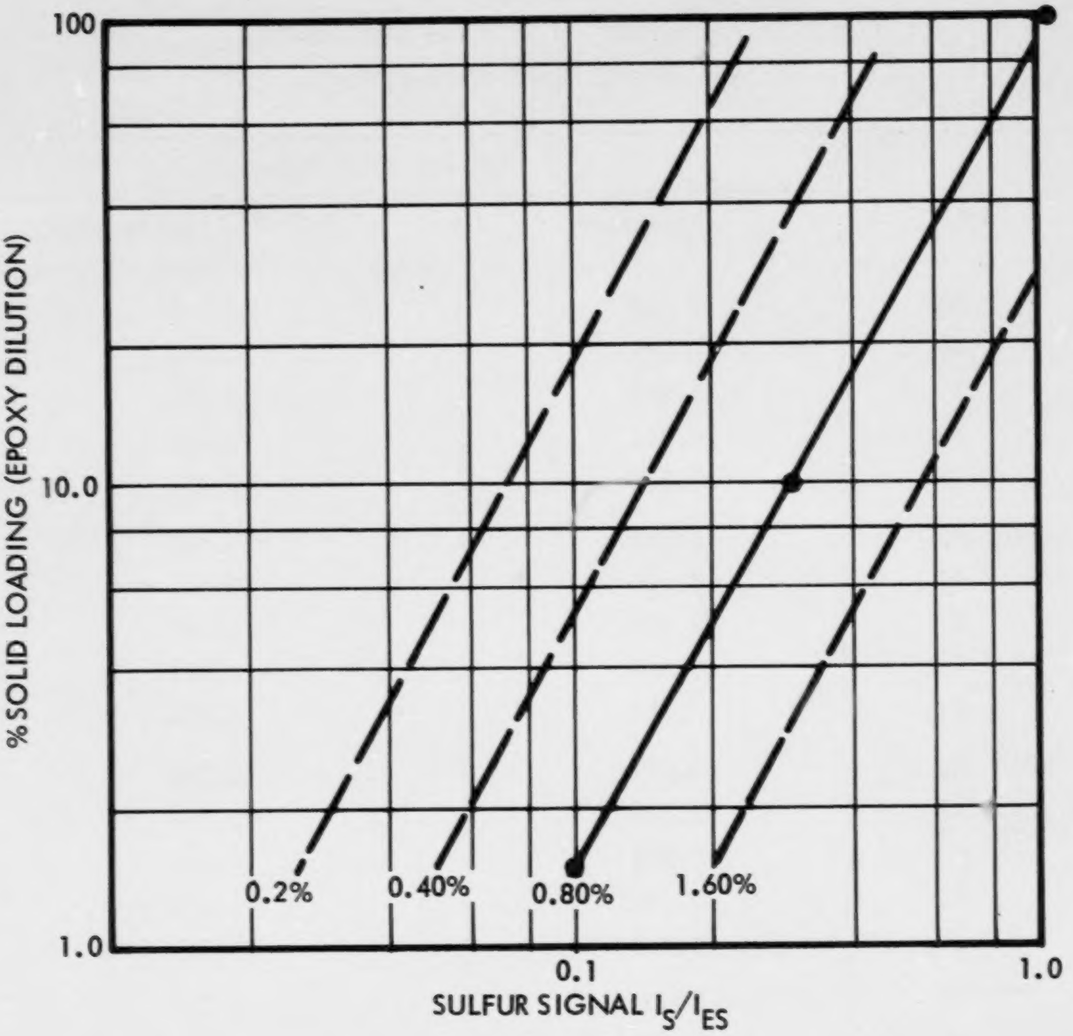

Figure 13. Conceptual Concentration-Loading-Signal Map for Sulfur

every element except iron**, the X-ray intensity (voltage ratio) decreased when Kapton was introduced. The reduction was most severe for magnesium and this was expected because the magnesium radiation has the longest wavelength (hence, softest X-radiation). A comparison for sulfur was made between sample 004 (Limestone) and 005 (Limestone-7.9% w/w $CaSO_4$) under the

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**The slight increase in the iron signal may be due to the 30-100 ppm iron impurity which is frequently found in all grades of Kapton except the electronic grade.

TABLE XXVI
EFFECT OF KAPTON WINDOW ON X-RAY SPECTROMETER PERFORMANCE: 0.25-MIL SHEET

Sample		Voltage Ratio Values	
		No Kapton	0.25-Mil Kapton Sheet
002	Mg	0.212	0.148
	Al	0.019	0.010
	S	1.332	0.753
	Fe	0.422	0.463
	Ca	7.873	7.098
003	Mg	0.198	0.147
	Al	0.008	0.007
	S	2.666	1.351
	Fe	0.390	0.424
	Ca	7.412	6.670
004	Mg	2.879	0.285
(Lime-stone)	Al	0.168	0.041
	S	0.076	0.059
	Fe	1.279	1.294
	Ca	9.928	9.037
005	Mg	2.630	0.306
	Al	0.140	0.036
	S	2.052	1.000
	Fe	1.169	1.182
	Ca	9.354	8.512

two situations and the results were extrapolated to the case where a 1-mil Kapton window would be used. The results demonstrated that although the Kapton does degrade the performance of the unit, the detection limit with a 1-mil window is still below the 0.25% level (e.g., 0.20 % w/w).

3.2.8 Advantages of the ARL System

ARL claims at least two patented features of their Quantometer, an external standard to optimize system stability and a slurry density gauge. The external standard consists of a brass or titanium disc positioned to intercept a portion of the primary X-ray beam adjacent to the sample. The resulting non-dispersed X-ray signal is detected by a sealed detector. The detector output is integrated across a capacitor simultaneously with all other detector signals being measured, and is subsequently divided into the intensity values obtained in the elemental capacitors, hence, the I_s/E_{ES} outputs. This ratio technique is automated by terminating the overall integration period when the external standard capacitor reaches a predetermined fixed voltage (e.g., 4 volts). The slurry density gauge utilizes backscattered X-rays from the white spectrum to monitor changes in solids concentration. A curve of voltage from the scattered radiation channel *vs* wet specific gravity (measured as slurry density) is produced. The curve is good only for a slurry of a specific type. A major matrix change from lime concentrate to clay slime, for example, would require the use of different pulp density correction curves. Slurry density (or pulp density) correction curves must be generated for each element of interest.

The ARL PCXQ slurry unit is the recommended system for wet-scrubber on-line process monitoring of Ca, Mg, total sulfur and the other elements of concern. Its strong point is its proven ability to present and analyze slurry specimens. The weakness of X-ray fluorescence in general seems to be its sensitivity to specimen matrix, particle size, and slurry density. Corrections for these effects could be readily made with the aid of digital computer programs which are available from ARL. A discussion of multiple utilization of this computer for data acquisition and reduction of the output of other analytical instruments at the test site is presented in Section 4.

Solids Analyzer 2 and Solids Analyzer 3 shown in the design concept for continuous solids separation and analysis were originally considered as one XRF and one XRD unit. No commercially available on-line XRD unit has been found to date however, the concept is feasible with a dry powder presenter. As presently conceived, Analyses 1, 2 and 3 are three feed streams to the same XRF instrument. The advantage of this multi-stream approach is that totalsulfur and elements are determined in the composite slurry; after filtration (with or without solvent washing) and mild drying, major differences between dissolved and solid constituents may be estimated; and, finally, after pyrolysis for thermal removal of CO_2 from "available" carbonate and SO_2 from test labile sulfur species, the concentrations of Ca, Mg and other low level constituents are maximized in the solids to improve detectability and eliminate dilution and matrix effects. Automatic dry powder presenters for the last XRF channel are available from several sources. G.E. presents a slightly compressed, smoothed sample contained in a moving cup (XEG System) while ARL offers a briquetting unit for pelletizing the samples at 40,000 psi.

3.3 CONTINUOUS ON-STREAM CARBONATE ANALYSIS

It should be noted that in addition to demonstrating the utility of X-ray fluorescence in the continuous solids analysis system, Figure 10, the feasibility of the continuous thermal liberation of CO_2 from still "active" slurry solids with quantitative CO_2 measurement was amply demonstrated. Filtered, dried solids from the Demco cyclone efficiency tests (Section 3.1) (utilizing the spent Zurn slurry) were obtained from the overflow (to polishing filter for analyses requiring optical clarity) and underflow (to solids analyzer system). It will be recalled that although size classification occurs in the cyclone, the XRF analysis indicated no discernible compositional differences in the overflow and underflow solids. The carbonate values shown below tend to corroborate that conclusion:

		Carbonate Content, % w/w
Demco Overflow		57.0
		58.5
	Average	57.8
Demco Underflow		57.8
		57.0
	Average	57.4

These analyses, exclusive of separation and drying required approximately five minutes per test. The Leco laboratory unit provides simultaneous CO_2 and SO_2 elapsed analysis time of 60 seconds. Automation of Leco sample injection operations would provide an interesting alternative to XRF determinations which should take less time.

It is believed that continuous measurement or certainly consecutive batch sampling and determination of the available carbonate in the slurry scrubbing process will provide key process control information on the capacity of the spent stream and recycle stream that will permit maximum utilization of the slurry and thereby significantly improve process cost effectiveness.

3.4 DEVELOPMENT PLAN FOR WET SCRUBBER BISULFITE ANALYZER (WSBA) PROTOTYPE FABRICATION AND EVALUATION

With the completion of the laboratory development phase of the UV furfural bleaching method for sulfite, the next phase, i.e., to provide a preliminary design for automation of the procedure, was implemented. In order to support most effectively the 1972 start-up date for the EPA Limestone-Wet Scrubber Test facility at Paducah, Kentucky, the plan for provision of a sulfite method has been first to provide a detailed instrumental method, which has been accomplished (see Appendix E), and second, to design a batch automated type analyzer for laboratory utilization. The objective is to provide the most economic procedure in terms of 1) speed and simplicity of performance, 2) maximum versatility, and 3) ease of implementation.

A flow diagram design of the batch automated analyzer to meet these objectives is presented in Figure 14. This design is based on the following considerations to achieve complete automation with attainable required analytical accuracy:

- Sampling system: a dual sample system that has a 9-minute time cycle for each sample position is required. The dual system is to have a 4.5-minute overlap between samples yielding an initial throughput capacity of approximately 100 samples/shift. This can easily be doubled or tripled at a later time.

- Sample dilution ratios: the optimum ratios for a 2 dilution system are approximately 17:1 for the reagent add stage of the low concentration sample, and 170:1 total dilution for the high concentration sample.

- Bleach development time: a minimum development time appears to be around 5 or 6 minutes.

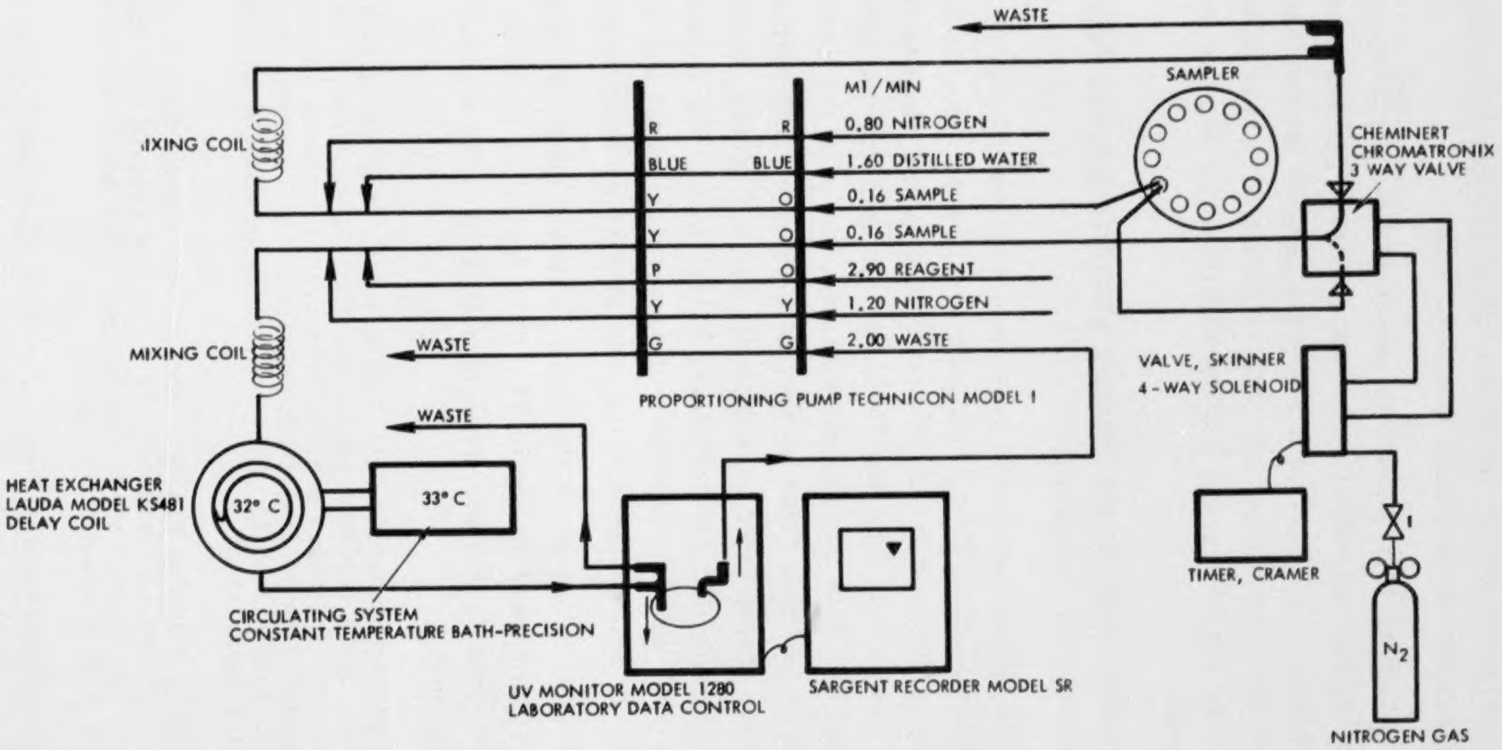
WASTE
SAMPLER
Ml / MIN
0.80 NITROGEN
1.60 DISTILLED WATER
0.16 SAMPLE
0.16 SAMPLE
2.90 REAGENT
1.20 NITROGEN
2.00 WASTE
R
BLUE
Y
Y
P
Y
G
R
BLUE
O
O
O
Y
G
CHEMINERT
CHROMATRONIX
3 WAY VALVE
IXING COIL
MIXING COIL
WASTE
WASTE
PROPORTIONING PUMP TECHNICON MODEL I
VALVE, SKINNER
4-WAY SOLENOID
HEAT EXCHANGER
LAUDA MODEL KS481
DELAY COIL
32° C
33° C
CIRCULATING SYSTEM
CONSTANT TEMPERATURE BATH-PRECISION
UV MONITOR MODEL 1280
LABORATORY DATA CONTROL
SARGENT RECORDER MODEL SR
TIMER, CRAMER
1
N2
NITROGEN GAS

Figure 14. WSBA Flow Diagram

- Temperature: 5% error band is induced by a 1.2°C change in temperature.
- Analyzer cell: the cells must be temperature controlled and be capable of having prior samples pumped out.
- Spectrometer: a dual beam grating or prism instrument with a reproducibility in transmission units of approximately 0.2% at 276 *nM* is required (a line source at 276 *nM* could also be used).

Recommended future studies will concentrate initially on factors to evaluate the selection of the parastaltic pump. These studies will determine the dilution and reagent addition steps, and flexible tube stability. The first experiments will investigate the dead space and mixing effects of the total system under test. Subsequently, a study of temperature effects will be conducted with the pump and reagents at 22°C and 40°C using various dilutions with primary emphasis on the 17:1 dilution ratio.

In addition, it is recommended to determine the extent of detector error through repetitive calibration runs (e.g., five samples, five times for five different days). Premixed standards will be used for all tests. In addition, other experimental parameters will be assessed individually, such as flow - stop flow in the UV cell, temperature controller, dilution ratio, mix chamber, bubble rate, furfural adding, and sample adding effects. When the extent of individual factors have been determined, the key output-dependent characteristics will be varied in the total system to determine whether the continued effects are additive. The magnitude of these error effects will be quantitized through statistical treatment of the data.

3.5 BENCH SCALE WET SCRUBBING PROCESS SIMULATOR

A modular bench scale test loop wet scrubber was designed and fabricated to permit evaluation of the recommended methods under simulated use conditions. A loop system was selected because of the necessity of: 1) closely approximating the full scale operating unit, 2) accurate control, and 3) producing stable (equilibrium) and unstable (non-equilibrium) conditions for evaluating candidate instrumental methodology under known, controllable conditions with realistic compositions. A schematic diagram is presented in Figure 15 while a photograph of the fully assembled system is shown in Figure 16.

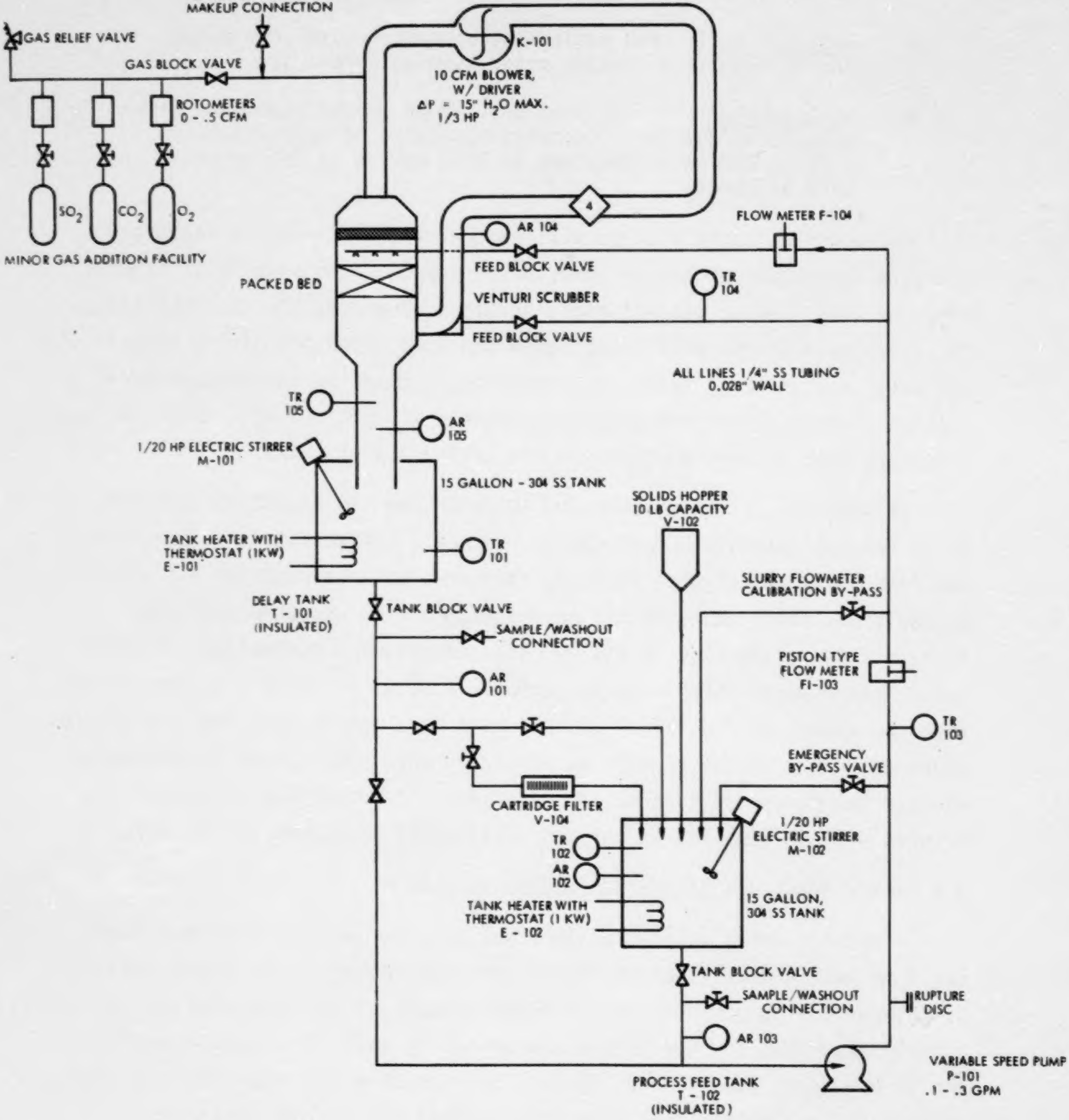
GASEOUS NITROGEN
MAKEUP CONNECTION
GAS RELIEF VALVE
GAS BLOCK VALVE
ROTOMETERS
0 - .5 CFM
SO2
CO2
O2
MINOR GAS ADDITION FACILITY
K-101
10 CFM BLOWER,
W/ DRIVER
ΔP = 15" H2O MAX.
1/3 HP
4
AR 104
FEED BLOCK VALVE
FLOW METER F-104
PACKED BED
VENTURI SCRUBBER
TR
104
FEED BLOCK VALVE
ALL LINES 1/4" SS TUBING
0.028" WALL
TR
105
AR
105
1/20 HP ELECTRIC STIRRER
M-101
15 GALLON - 304 SS TANK
SOLIDS HOPPER
10 LB CAPACITY
V-102
TANK HEATER WITH
THERMOSTAT (1KW)
E-101
TR
101
DELAY TANK
T - 101
(INSULATED)
TANK BLOCK VALVE
SLURRY FLOWMETER
CALIBRATION BY-PASS
SAMPLE/WASHOUT
CONNECTION
PISTON TYPE
FLOW METER
FI-103
AR
101
TR
103
EMERGENCY
BY-PASS VALVE
CARTRIDGE FILTER
V-104
1/20 HP
ELECTRIC STIRRER
M-102
TR
102
AR
102
15 GALLON,
304 SS TANK
TANK HEATER WITH
THERMOSTAT (1 KW)
E - 102
TANK BLOCK VALVE
SAMPLE/WASHOUT
CONNECTION
RUPTURE
DISC
AR 103
VARIABLE SPEED PUMP
P-101
.1 - .3 GPM
PROCESS FEED TANK
T - 102
(INSULATED)

Figure 15. Bench Scale Scrubber Analysis Loop

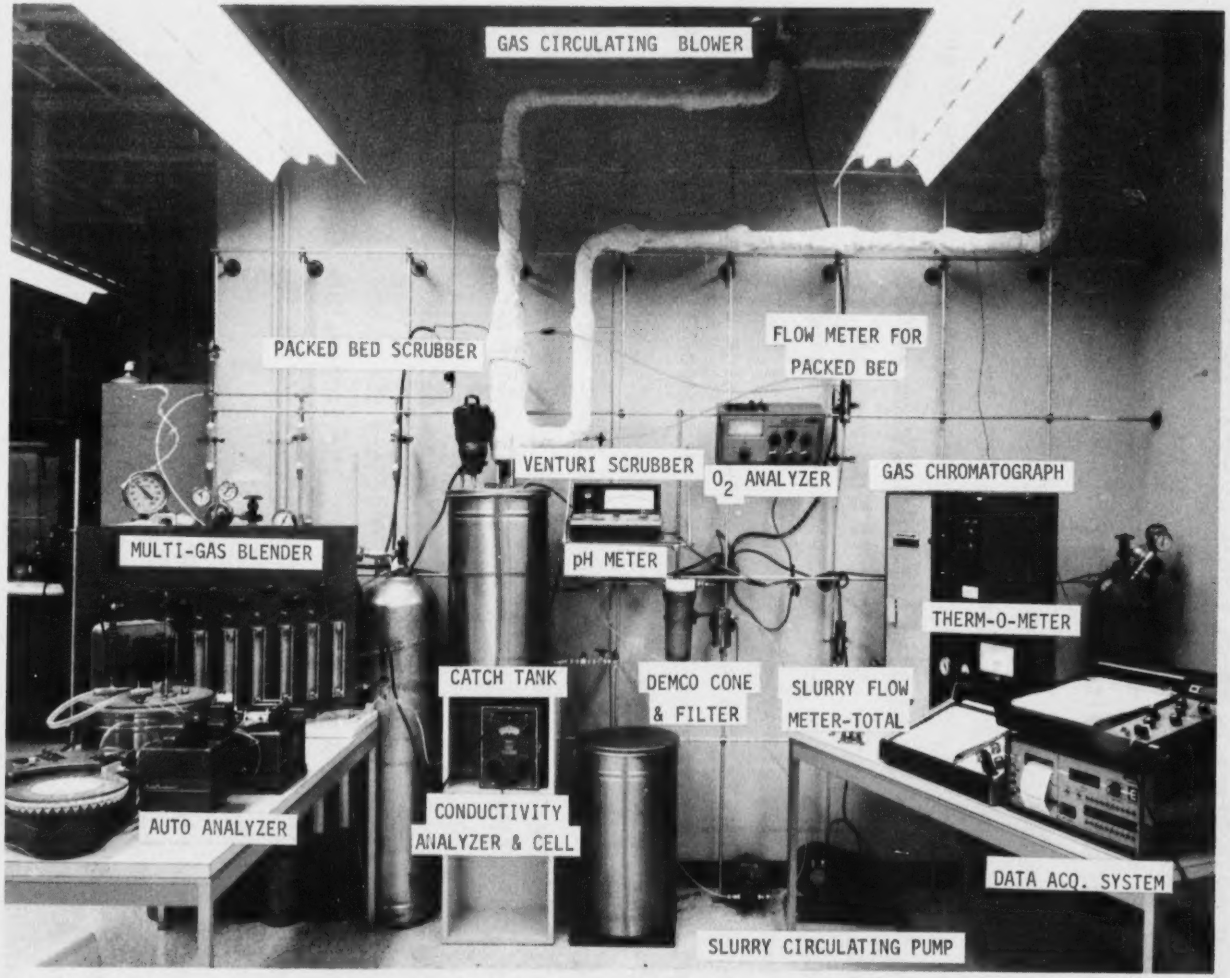
GAS CIRCULATING BLOWER
PACKED BED SCRUBBER
FLOW METER FOR PACKED BED
VENTURI SCRUBBER
O_2 ANALYZER
GAS CHROMATOGRAPH
MULTI-GAS BLENDER
pH METER
THERM-O-METER
CATCH TANK
DEMCO CONE & FILTER
SLURRY FLOW METER-TOTAL
CONDUCTIVITY ANALYZER & CELL
AUTO ANALYZER
DATA ACQ. SYSTEM
SLURRY CIRCULATING PUMP

Figure 16. Photograph of Instrumented Bench Scale Process Scrubber Simulator

The system consists of a bench scale Venturi scrubber with a second stage packed bed, fitted with a recirculating gas stream. The pressure drop associated with the packed bed is about 0.5-inch of water, the pressure drop due to the Venturi is about 1 inch of water and the pressure drop associated with the ducting is 0.4-inch of water. The packed bed is 9-inch deep and has a diameter of 4-inch. The ducting is 2-inch I.D. throughout. The Venturi has a throat size of 1 inch.

The recirculating gas stream is moved via blower K-101. The composition of the recirculating gas stream is controlled by the Minor Gas Addition facility. This facility allows the addition of small amounts of gases *via* rotometers and bottled gas. Gases such as SO_2, CO_2 and O_2 are controlled in this manner. Nitrogen is bled into the system to make up that amount which has been absorbed by the circulating slurry and maintain a positive inert gas blanket. The level of slurry in the liquid separator V-103 is controlled in this manner. The composition of the gas stream is monitored by gas analyzer AR-104, which gives compositions of SO_2, CO_2 and O_2 in the circulating stream.

The liquid slurry exits the Venturi scrubber *via* the liquid separator V-103. The temperature in the downcomer is measured and recorded by TR-105. Analyses of the slurry can be provided in the downcomer by tapping a port for analyzer AR-105. The liquid stream from the liquid separator dumps into a 15-gallon delay tank (T101), where it is agitated with a 1/20 horsepower electric laboratory stirrer (M-101), and the temperature is adjusted and controlled by a tank heater (E-101). The temperature is measured and recorded by TR-101. The residence time in this delay tank is about one hour with a design slurry flow of 0.2 gpm.

The liquid slurry travels to the process feed tank along one of two routes. It can travel along the straight transfer section, or it can be diverted through a filter. The purpose of the filter is to take out solids from the circulating slurry. The composition of the slurry exiting the delay tank is monitored and recorded by AR-101.

The solids content of the slurry in Process Feed Tank (T-102), a 15-gallon, 304 stainless steel tank equipped with a 1/2 horsepower laboratory stirrer, is adjusted by adding limestone from the solids hopper. The composition of the tank is monitored and recorded by the process analyzer AR-102. The temperature in this tank is maintained by tank heater E-102 and is measured and recorded by TR-102.

The adjusted slurry from T-102 is transported along the transfer line with a positive displacement pump, P-101. This pump has the capacity of 0.1 to 0.3 gpm. This range is required so that the liquid to gas ratio present in the packed bed Venturi scrubber is capable of being changed. Accurate flow of the pump output can be adjusted *via* the recycle stream to T-102. The temperature in this section of line is recorded on TR-103. The flow then splits, part going through the counter-current flow section of the packed bed. The other part of the flow goes to the throad of the Venturi. The flow which goes to the packed bed section is measured on flow indicator FI-104, while the flow to the Venturi scrubber is determined by difference utilizing the flow monitored on flow indicator FI-103.

All liquid lines present in the bench loop simulator are of 1/4-inch polypropylene, with an 0.028-inch wall. Utilizing this type of tubing, the flow velocity is about 1.8-feet per second.

This unit has been used to test the applicability of the recommended methods under controlled conditions, as described below. For this series of experiments the process feed tank (T-102) was by-passed from the delay tank (T-101) directly to the variable speed slurry pump (P-101). Continuous pH measurement of scrubber effluent from the Venturi downcomer was accomplished in the 15-gallon delay tank (T-101) by means of a combination electrode connected to a Corning Model 12 research pH meter. Readout was monitored continuously on a strip chart recorder. This may be considered in-line analyzer AR-105. For a brief description of available process pH monitoring equipment see Section 3.6 and Appendix G.

Initial check-out and operation with gaseous SO_2 feed and limestone slurry (3.6% w/w solids) revealed three mechanical problems that were rectified prior to proceeding to demonstrating proposed method applicability and varying processing parameters. The first difficulty was associated with the 10 cfm gas circulation blower (K-101) which utilized air intake to cool the motor. It was necessary to seal the blower and provide external cooling. In the slurry circulation check-out run, the phenolic impeller of the Flowtek, Inc., circulation pump P-101 split in half, aborting the run after one hour of operation. After replacement and continuous operation of the replacement impeller, it was examined, showing considerable abrasive wear. Because no rubber or stainless steel replacement impellers were available, this pump was replaced in favor of a Jabsco pump with rubber impeller. The last modification to the scrubber was required in the packed bed packing material which initially was Raschig rings. This bed packing tended to collect and accumulate slurry solids to the point of flow stoppage. This problem was remedied by replacing the Raschig rings with large rings (3/4-inch O.D. x 1-inch long) made from PVC pipe.

The following paragraphs describe the experiments that were performed to determine 1) the inherent oxidation effect of the scrubber system in the absence of oxygen and flyash, and 2) demonstrate the utility of the recommended procedures. Additionally, several scrubber experiments were performed through in-house support to examine the effect of temperature, flyash and oxygen.

3.5.1 Bench Scale Scrubber Tendency for Slurry Oxidation

To establish the system baseline tendency for oxidation of sulfite to sulfate, prior to flue gas, flyash, limestone or oxygen addition, the bench scrubber was charged with 10 liters of deionized, deaerated water prepared by nitrogen sparging and 6.244 g $NaHSO_3$ reagent ($\sim$6 *mM*). A zero time sample (blank) was taken from the catch tank prior to slurry circulation. Samples (100 ml) were taken every 15 minutes for the two-hour duration of the experiment. A positive pressure or blanket of inert N_2 gas was maintained throughout the test. The pH of the catch tank was determined by monitor AR-105. Table XXVII presents the results of the analyses for bisulfite ion as well as the pH of the catch tank solution at the time each sample was taken. The data correlates very well between pH and the apparent sulfate formed from oxidation. Elapsed time for the sulfite analysis by the laboratory instrumental method (Appendix E) was approximately five minutes for the time of sampling whereas the furfural/buffer addition was performed immediately upon sampling. More important than gaining experience and confidence in the methods was establishing the baseline behavior

TABLE XXVII

BISULFITE ANALYSIS FOR BISULFITE OXIDATION BENCH SCRUBBER EXPERIMENT 104

No.	Time, Min.	HSO_3^- Conc., *mM*	S(IV) Removed	pH
0	0	5.85	-	4.95
1	15	5.50	6	4.00
2	30	5.10	13	3.85
3	45	4.69	20	3.75
4	60	4.32	26	3.70
5	75	4.14	29	3.60
6	90	3.93	33	3.60
7	105	3.54	40	3.50
8	120	3.29	44	3.40

of the scrubber system to help elucidate the results of the forthcoming experiments. At the present time it is only possible to point out several possible causes for the observed oxidation phenomenon. They may include surface oxide coating, residual dissolved oxygen and last, perhaps most significant phenomenon, the spontaneous decomposition of bisulfite reported by Chertkov (Reference 18) as follows:

$$4HSO_3^- \rightarrow S_3O_6^{2-} + SO_4^{2-} + 2H_2O \qquad (22)$$

The formed trithionate then hydrolyzes to yield more sulfate and thiosulfate which then reacts with an intermediate HSO_3 radical to yield more trithionate:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (23)$$

$$HSO_3 + OH + HS\cdot HSO_3 \rightarrow (HSO_3)_2\cdot S + H_2O \qquad (24)$$

The possibility that added sulfur (as SO_2) was being lost to the system walls in a passivation process rather than the more probable oxidation or disproportionation reactions described above was investigated further. A second sodium bisulfite run was conducted with an approximate charge of

6 *mM* HSO_3^-. Both bisulfite and total sulfur as sulfate* were determined every 15 minutes over a two-hour period of recirculation. Oxygen was added after the first hour of operation. After the first hour the sulfite decreased from 6 *mM* to ∿3 *mM* (∿50% decrease) and at the conclusion of the second hour the sulfite level was 1.5 *mM* (∿75% decrease). Total sulfur in solution remained essentially unchanged throughout.

3.5.2 Evaluation of Recommended Methods for Characterization of the Limestone Scrubber Process

The two experiments described in this section, utilizing the bench scale wet scrubber loop with fresh TVA limestone and gaseous SO_2, were directed specifically toward demonstration of the utility of the developed WSBA method and applicability of atomic absorption spectroscopy and pH monitoring.

3.5.2.1 Standard Operating Procedure for Bench Scale Scrubber - In each of the experiments described in this section as well as those in the following Section 3.5.3, the procedure for charging the scrubber, feeding the simulated flue gas and operating the process were very nearly identical. They were as follows:

> Three pounds of screened (less than 30 mesh) TVA feed limestone was added to 10 gallons of nitrogen-sparged, deionized water in the process run tank and mixed. The feed pump was then started and the flow adjusted to run conditions, 0.1 gpm through the Venturi scrubber and 0.1 gpm through the packed bed scrubber. The blower was then started and sulfur dioxide was introduced at a flow rate of 0.015 cfm. The sulfur dioxide addition was continued for a period of 45 minutes and then terminated. The circulation of the gas system at approximately 12 cfm was continued for 75 minutes more, with the addition of 0.0177 CFM nitrogen. One hundred milliliter samples of the slurry mixture were taken from position AR 101 at the start of the experiment (before SO_2 flow) and every 15 minutes thereafter. The samples were immediately filtered through two Whatman 41 filter pads while under a nitrogen blanket maintained by a flow of dry GN_2. The clear filtrates were collected and one aliquot analyzed immediately for bisulfite ion [total S(IV)]

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*Total dissolved sulfur values were obtained by oxidation of the aliquot with 3% hydrogen peroxide, precipitation with barium chloride and gravimetric determination of the barium sulfate.

using the furfural bleaching method. Atomic absorption analysis for cations was performed on a separate aliquot of the filtered sample. The pH was continuously monitored using AR 105, previously described.

3.5.2.2 Results of Characterization of Scrubber Slurries - The two scrubber experiments were designated Runs No. 105 and 106 and were identical with the exception that No. 106 incorporated an oxygen addition at the 180 min elapsed run time and involved more comprehensive characterization for comparison to process parameter variation runs detailed in Section 3.5.3. The data obtained for these runs are shown in Table XXVIII.

TABLE XXVIII

BISULFITE ANALYSIS FOR THE LIMESTONE SLURRY

BENCH SCALE SCRUBBER EXPERIMENTS

No.	Time Min.	pH #105	pH #106	Bisulfite (mM) #105	Bisulfite (mM) #106	Total Sulfur in Solids (g) 106	Total Sulfur in Filtrate (mg), 106	Fe in Filtrate ppm, 106	Ca in Filtrate mM, 106
0	0	9.40	9.50	0	0	-	-	-	
1	15	7.30	7.45	1.25	1.19	-	-	-	
2	30	6.85	6.90	2.67	2.19	--	-	<0.1	
3	45	6.65	6.60	3.31	2.81	2.6	12.8	<0.1	5.16
4	60	6.65	6.60	1.53	2.22	-	-	<0.1	4.81
5	75	6.65	6.65	1.74	1.68	-	-	-	5.30
6	90	6.70	6.70	1.45	1.51	-	-	-	
7	105	6.70	6.70	1.39	1.39	-	-	-	
8	120	6.80	6.75	1.10	1.24	-	-	-	
9	180		6.95		0.69	-	6.6	<0.1	4.71
	Oxygen flow started after Sample 9 taken								
10	315		7.50		0.03	8.0		<0.1	
11	390		7.70		0.10	8.9	7.2	-	

The results available for comparison between Runs 105 and 106, i.e., through a run time of 120 min for bisulfite and pH, show very good agreement. The significance of this finding is that the run parameters are stable and controllable with the TRW bench scale design and, in addition, that 1) the WSBA laboratory instrumental method is an improvement over currently available methodology, and 2) automation will provide further economic advantage.

It should be noted that the continual loss of sulfite through this point in the scrubber operation remained perplexing. The process parametric study discussed in the next section provided invaluable information on at least one important phenomenon contributed to this loss and that may be an important factor in the TVA operation.

3.5.3 Study of Wet Scrubber Process Variables Using the TRW Bench Scale System

As described above, the bench scale limestone scrubber unit was successfully used to demonstrate the utility of the recommended analytical procedures for rapid characterization of filtered limestone slurry mixture composition. The additional studies described below were conducted at TRW through partial in-house support, and although these studies are beyond the scope of the current program, they are reported because they 1) are relevant to the chemistry of limestone scrubbing processes, and 2) clearly identify future areas of technical endeavor required for detailed elucidation of the significant processes needed for systematic process design improvements.

3.5.3.1 Experimental - The bench scale limestone scrubbing process simulator was used exclusively in these experiments. Figure 16 shows the unit with associated heat-traced lines and analysis instrumentation located nearby to facilitate rapid analyses. In these experiments, sampling was accomplished by periodic removal of 100-milliliter samples of the slurry mixture from the sampling point AR 101, rather than using the recommended continuous Demco/polishing filter approach (because of the high liquid flow requirements of the latter unit).

In these experiments, operating temperature, fly ash and oxygen were variables evaluated for their influence on the limestone scrubber chemistry. In these studies the total solids loading was maintained at 3.1 to 3.6% w/v. When limestone/fly ash mixtures were employed the limestone content was 2.5% w/v and the fly ash content was 0.6% w/v. Because insufficient TVA fly ash was on hand for the entire series of experiments, it was decided to use the available fly ash from Nevada Power Plant, Moapa, Nevada. However, its chemical composition was considerably different than that previously obtained from the Shawnee Power Plant, Paducah, Kentucky. Consequently, it was modified by addition of oxides of iron, cobalt and nickel to bring its metal composition to values directly comparable to that of the Shawnee Power Plant fly ash. In addition, the Moapa fly ash was considerably more basic than that from the Shawnee Power Plant, hence, the charge was neutralized (in a slurry form) to pH 7 with hydrochloric acid prior to system addition. In this way, the pH of the system during sulfur dioxide addition was maintained between 6.3 and 7.8, which is representative of operational units of the Kansas Power and Light Company and the Key West Electric Company.

The general operating procedure consisted of charging the reservoir with 12 gallons (45.5 liters) of deionized water, adjusting the temperature to the desired level and deaerating the water by sparging it with argon gas and stirring it for two hours. Limestone and neutralized fly ash slurry were added as desired for the experiment. Gas phase preparations consisted of heating the system to the desired temperature and purging it with nitrogen gas maintained at a flow rate of 0.018 cfm. At the beginning of the run, slurry pumping through both the flooded bed and Venturi scrubber was initiated and then sulfur dioxide was introduced into the system at a flow rate of 0.015 cfm (at 22°C). After 45 minutes, the sulfur dioxide feed was terminated and the nitrogen gas flow was allowed to continue throughout the remainder of the experiment to preclude any oxygen pick up from the surrounding environment. Subsequent mass spectroscopic analysis of the reagent grade sulfur dioxide gas revealed an assay of only 86% v/v with the remainder consisting of air. Therefore, the 45-minute addition of sulfur dioxide resulted in introduction of a total analytical concentration equivalent to 15.0 *mM* S(IV) present in the 45.5 liters of slurry. The corresponding oxygen content introduced during sulfur dioxide addition was 0.48 *mM* O_2. These values are true as well for Runs No. 105 and No. 106 above, but the quantity of oxygen added with the SO_2 does not account for the bisulfite loss. In Run 112, when oxygen was added deliberately to the system, the nitrogen feed was reduced to 0.014 cfm and oxygen was added at a rate of 0.004 cfm (resulting in a total oxygen content equivalent to 5.46 *mM*, if soluble in the 45.5 liters of slurry). On termination of the sulfur dioxide and O_2 feed after 45 min in Run 112, the nitrogen feed rate was increased to 0.018 cfm.

As mentioned previously, 100-ml aliquots of the slurry were taken from the delay tank prior to sulfur dioxide introduction and every 15 minutes after experiment initiation. The samples were filtered immediately through a Whatman 42 filter paper under a nitrogen-purged plastic dry bag. The clear filtrates were collected in 100-ml volumetric flasks and then analyzed within two minutes of sampling for bisulfite ion [total S(IV)] using the furfural bleaching method. The pH was monitored continuously at AR 105 using the Corning Model 12 pH meter and a combination electrode coupled to a strip chart recorder. Selected filtrate samples were analyzed for total sulfur content (peroxide oxidation followed by barium ion precipitation) and total calcium ion content (atomic absorption).

3.5.3.2 Results - The findings of these experiments were somewhat surprising. Figure 17 shows typical smoothed curves for liquor bisulfite ion concentration as a function of time. At room temperature (Run 106), it is seen that approximately 20% of the available sulfite is retained in the liquid phase and that after sulfur dioxide addition, there was a monotonic decrease in bisulfite ion as a function of time. Initially, it was believed this decrease originated principally from air oxidation of the bisulfite; however, inspection of the data reported in Table XXIX for analysis of the sulfate [S(IV)] content of these solutions shows that the sulfate content did not change appreciably during the experiment. This finding suggests that the slow, continual reduction in bisulfite originates from precipitation of calcium $CaSO_3 \cdot 1/2H_2O$ (which was observed by X-ray diffraction to be the only sulfur-containing species in the solid phase).

Another interesting finding was that the sulfate sulfur increased significantly (2-3 fold) and associated sulfite content decreased when fly ash was added. This observation suggests enhanced oxidation of sulfite through catalysis by trace fly ash metal ingredients. Because the extent of oxidation is considerably more than that capable through direct combination with the available dissolved oxygen (0.48 *mM*), it appears that some reduction of the metal oxides or salts may also take place or that the bisulfite disproportionation is significantly enhanced through catalysis.

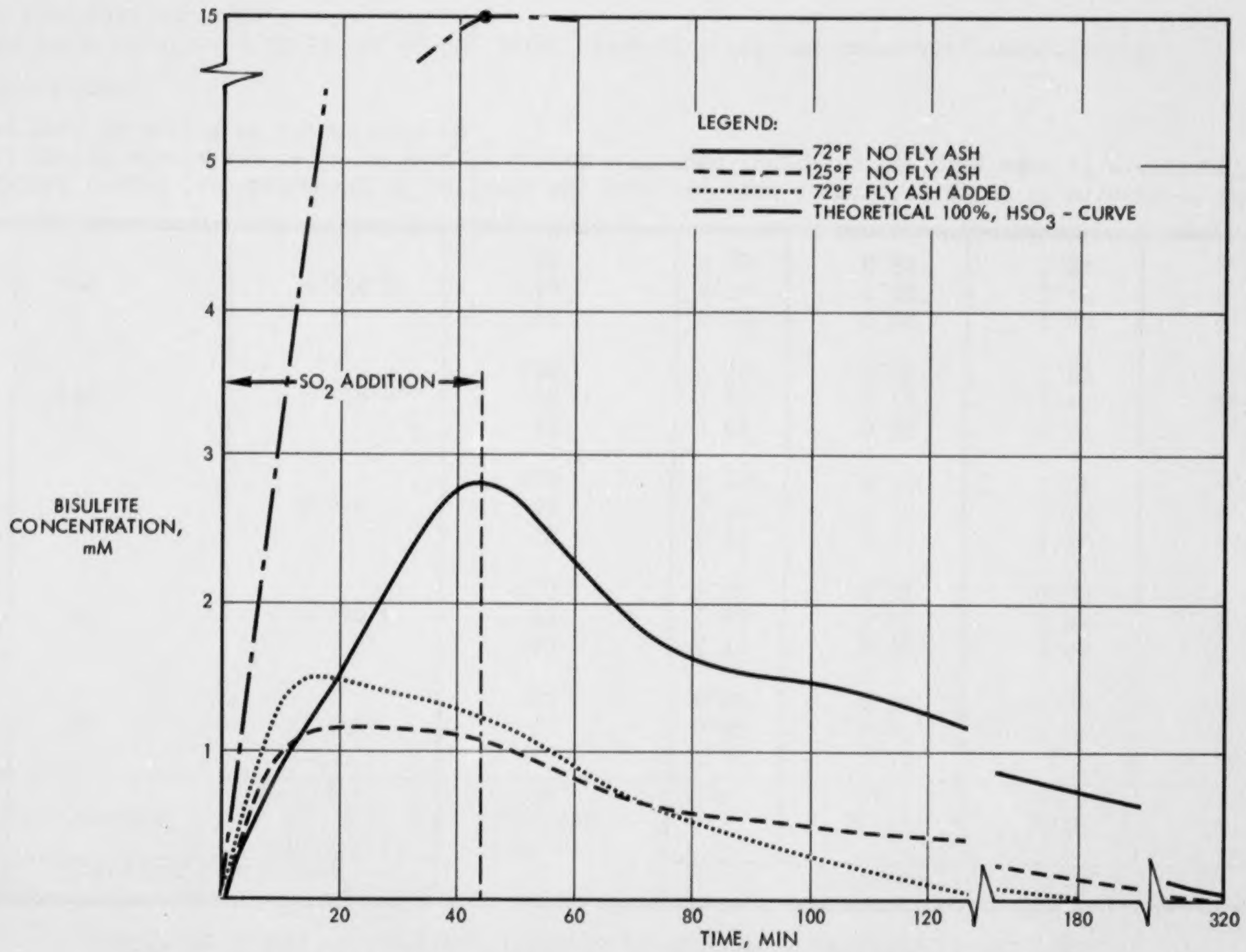

Figure 17. Effect of Fly Ash and Temperature on Soluble S(IV) in Bench Scale Wet Scrubber

TABLE XXIX

LIMESTONE SLURRY LIQUOR COMPOSITION AS A FUNCTION OF OPERATING CONDITIONS AND TIME

Run	Operating Conditions[a]		Time of Sampling Min.	Filtered Liquor Composition			
	Temperature °F	Limestone/ Fly Ash % w/v		pH	S(IV), *mM*	S(VI), *mM*	Total Calcium *mM*
106	72	3.6/0	15	7.45	1.19	b	b
			45	6.60	2.81	1.19	5.16
			180	6.95	0.69	1.38	4.71
110	72	2.5/0.6	15	6.70	1.49	3.06	8.73
			45	6.60	1.22	2.95	9.35
			120	6.60	0.12	3.25	7.98
113	125	3.6/0	15	6.70	1.15	1.16	3.24
			45	6.35	1.15	1.18	4.11
			105	6.70	0.50	1.06	2.87
111	125	2.5/0.6	15	7.65	0.86	2.07	7.73
			45	7.15	0.74	2.19	7.73
			120	7.45	0.09	2.53	7.48
112[c]	125	2.5/0.6	15	6.90	0.96	2.60	8.23
			45	6.75	1.01	2.42	8.98
			105	6.85	0.66	2.34	8.73

[a] Continuous closed loop scrubbing of influent SO_2 gas; SO_2 feed terminated after 45 minutes of addition [total charge equivalent to 15 *mM* S(IV)]; system continued recycling for remainder of experiment with N_2 gas feed to ensure no oxygen pick-up.

[b] Not determined.

[c] Oxygen added together with SO_2 at O_2/SO_2 molar ratio of 0.267 and terminated concurrently after 45-minute addition.

Comparison of Run 113 with 106 and Run 110 with 111 permits evaluation of effect of temperature. The observation that increased temperature reduces the sulfite content is explained through enhanced $CaSO_3 \cdot 1/2H_2O$ precipitation kinetics. It is believed that the lower sulfate content at elevated temperature was caused by lower solubility of oxygen, which, of course, controls the kinetics of oxidation.

In the experiment when a significant quantity of oxygen was added (Run 112) its affect appears to be of second order magnitude. A significant higher quantity of sulfate was observed compared to its corresponding Run 111, however, the sulfate content was observed to decrease as a function of time suggesting either 1) calcium sulfate coprecipitation within the calcium sulfite hemihydrate, or 2) a poorly mixed sample.

Another expected finding was that the fly ash introduced a considerably higher soluble calcium into the slurry than the limestone. This stems from the fact the fly ash calcium form is the more soluble calcium oxide (hydroxide) and in our case that was partially titrated with hydrochloric acid.

It should be noted that the products of the total calcium ion and the total bisulfite ion concentrations readily exceed by two orders of magnitude the solubility product of calcium sulfite hemihydrate (8.4×10^{-8}) whereas the products of the total calcium and total sulfate ion concentrations are of the same magnitude as the solubility product of the calcium sulfate dihydrate (2.4×10^{-5}) inferring that under the conditions of the experiment calcium sulfite hemihydrate precipitates and calcium sulfate dihydrate does not. It is recognized that this simple calculation did not take into account considerations of activities of the ions and the distribution of the analytical concentrations in other species, such as $CaSO_3^\circ$, $CaHCO_3^+$, $CaSO_4^\circ$, and $CaCO_3^\circ$.

An attempt was undertaken to provide a detailed compositional analysis using the data of the Radian Corporation (Reference 2), however, on extensive evaluation of that work it became obvious that the many assumptions used in generating the thermodynamic disassociation constants and variations as a function of temperature, together with total disregard of known thionate chemistry equilibria in this media, would make the results of such calculations open to considerable question. In addition, the concentration of some of the input materials in our experiment (e.g., acid needed to neutralize the fly ash) were known only semiquantitatively, hence, calculation of the ionic strength employed was not well-established. Consequently, the theoretical analysis was abandoned at this time, however, it is clear that additional effort is warranted in this area, particularly for generation of fundamental or "effective" constants under use conditions of elevated temperature, solids loading, and non-equilibrium conditions.

3.5.3.3 Recommendations - As is seen from the previous discussion, laboratory bench scale experiments can be very useful in elucidating the chemistry involved in the wet limestone scrubbing sulfur dioxide abatement process. The bench scale studies permit studying a wide range of well-controlled operating conditions in a relatively short time and at considerable lower cost than full scale process unit. Consequently, it is recommended that bench scale studies be conducted to augment and complement full scale tests by identifying the more significant parameters for detailed testing thereby reducing the need and, hence, the cost of extensive full scale evaluation.

The significant finding observed in the tests reported above, namely, the rate dependent step in holding tanks having controlled environments is that of calcium sulfite precipitation, should not be under emphasized. The rate of precipitation could control the effectiveness of sulfur dioxide absorption in full scale scrubbers operated at pH 6-7. It is clear that near term bench scale studies of this type are warranted in which detailed material balances are made, together with use of operating conditions which closely represent full scale operational ranges. Findings from these studies will permit 1) early fixing of operational ranges, 2) identifying conditions leading to problem areas such as scaling, erosion, etc.), and 3) improved scrubber design and operational modes.

3.6 PROCESS MONITORING FOR pH

On stream pH monitoring devices applicable for wet limestone scrubber systems have been reviewed. Of those available on the market, three candidate systems, manufactured by Beckman Instruments, Universal Interloc, Inc., and Leeds and Northrup, have been selected for recommendation. Appendix G lists the specifications, available materials of construction, special features and costs. Both Beckman and Universal Interloc produce second generation amplification systems for pH readout; the main improvement results from the differential amplification of the glass and reference signals eliminating ground loop interferences. Mechanical strength is a very important factor in the final selection of a system. The availability of electrodes constructed of non-scaling or non-fouling material should be considered. In scaling studies performed at TRW, Teflon was found to be superior to other polymers and metals and should be used whenever possible.

4.0 TASK III - DATA ACQUISITION AND PROCESSING

The purpose of this task was to identify data collection and reduction methodology that will be suitable for computer input. Data format or instrument signal must be capable of interfacing with the eventual engineering computational system to be operational at the TVA wet scrubber plant site.

Depending upon 1) the mode of operation of the analytical instrumentation, i.e., laboratory or on-line, 2) the allowable elapsed time from sampling-to analysis-to data hard copy, i.e., real-time data output versus delayed batch data handling, and 3) the funds available and appropriate cost trade-offs that must be made from a position of total project overview, several degrees of sophistication of data acquisition systems are possible. Three alternative systems are described below. The computer data acquisition system associated with the recommended XRF on-line process instrument is the primary candidate system because of its proven application for similar analyses and availability to meet the demonstration start schedule at TVA.

4.1 COMPUTER DATA SYSTEM FOR XRF ON-LINE PROCESS INSTRUMENTATION

The recommended on-line continuous slurry analyzer for calcium, magnesium, total sulfur and other selected elements, as described in Section 3.2, is the ARL PCXQ 4400 XRF unit. Likewise ARL's laboratory XRF instruments were considered excellent candidates for laboratory analysis. These systems are equipped with a Hewlett-Packard 2114C computer as a standard option. Discussions were held with ARL technical sales personnel to determine the basic computer configuration, its utilization by the XRF unit and its potential for monitoring other laboratory or on-stream analysis instrumentation.

Table XXX describes the computer system recommended for the X-ray analysis function. Note particularly that the computer processor is available approximately 80% of the time the instrument is operating and is, of course, available totally when X-ray functions are not being performed.

The use of this computer for non-X-ray monitoring is limited primarily by the amount of computer memory (core) available, interfacing devices, and

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TABLE XXX

RECOMMENDED COMPUTER SYSTEM FOR XRF DATA ACQUISITION AND REDUCTION

Item	Hardware Configuration	Utilization by Quantometer
Computer	Hewlett-Packard 2114C	
	central processor	<20% of CPU time
	4K memory	50% to 100% depending on functions and instrument configuration
	16 I/O channels	2 or 3 channels (13 unused)
A/D Converter		Utilized only once (~1 sec) per sample to convert capacitor voltages (integrated counts) to digital values.
	SOFTWARE	
Sampling Program	supplied by ARL (core resident)	Collects and stores capacitor voltages (1 sec computer time/sample)
Quantitative Analysis	supplied by ARL (core resident)	Uses sample and standard values to compute weight percents of the various elements (5 sec computer time/sample).
Sample Selection	supplied by ARL (core resident)	Determine next sample for analysis (3-5 sec. computer time/sample)
Curve Fitting	supplied by ARL on tape. Must be read over other programs to use , then others reloaded.	Calculate new calibration curves by least squares

the availability of software to perform the required additional functions. If these are real limitations in the existing unit, they may be overcome by the purchase of additional equipment and programming services through ARL or Hewlett-Packard. Implementation of a system which performs non-X-ray functions, in addition to the X-ray analysis is a straightforward computer program development task.

4.2 ALTERNATIVE COMPUTER DATA PROCESSOR FOR GENERAL ANALYTICAL INSTRUMENTATION

General laboratory instrumentation data acquisition and processing systems may be designed around such highly sophisticated and costly computers as the IBM 1800 or Sigma 3. Assuming that such a system is not available, however, at Paducah, it would be much more cost effective to establish such a capability around a suitable minicomputer. As part of this task, the feasibility of the latter approach was investigated.

Recently, Digital Equipment Corporation (DEC), has introduced a general laboratory data processing system based on one of their minicomputers and compatible with various high data rate laboratory instruments. It is believed that this system, costing approximately $50K, unquestionably meets the needs of the laboratory and possesses the potential for process control as well.

The DEC PDP 12/LDP is designed as a simple-to-operate tool for a wide variety of real-time data-handling and research applications. Performance characteristics of the PDP 12/LDP have been optimized around a complete hardware/software system containing two processor modes identical to those on the widely used PDP 8/L and PDP-8/I. The Analytical Instrument Package includes all hardware for meaningful instrument/processor A/D interfacing. The Floating Point Processor allows high speed real time processing of data from high data rate instruments. The basic unit can accept data from four instruments simultaneously (expandable to sixteen instrument inputs at $1K/4 channels).

The PDP 12/LDP is a fully bundled system capable of sharing software programs (at no cost) from all PDP 12, PDP 8, LINC, and LINC-8 users through DEC's users group library (currently over 500 programs). This very important feature means that the system while big enough to handle the real-time processing requirements of high data rate instruments, such as mass spectrometry (MS) and fast Fourier transform infrared (IR) or nuclear magnetic resonance (NMR) spectroscopy, can also be used for process instruments and process control loops. Simplified programming languages are also available for special purpose programming by other than professional programmers. In addition, DEC has just opened an analytical instruments applications laboratory where they will continue to expand the available software for chemical applications.

A specific recommendation between the two choices of minicomputer systems available, i.e., DEC and HP, cannot be made at this time. Such a decision, as indicated previously, must be made based on overall project cognizance. However, if such a decision is pending, it is suggested that competitive bids be solicited from both vendors.

4.3 NON-COMPUTER DATA ACQUISITION

Non-computer data acquisition methodology is the last of the alternatives to be considered and, as the simplest, requires very little discussion. The principle recommended instrumental methods of analysis are X-ray fluorescence, atomic absorption, UV and NDIR spectrophotometry. Each instrumental output may be readily and inexpensively obtained in a variety of forms including digital, hard copy form directly in ppm or percent of species. For example, the ARL XRF unit is available with chart readout, typewriter, tape punch or tape printer as standard options. Multi-lamp AA units and spectrophotometers may be equipped with digital (BCD) output and linked through an appropriate logic board to the ARL data system for punch taping and/or printing. In this way data acquisition for quick look and manual computation is combined with computer interface capability.

5.0 CONCLUSIONS AND RECOMMENDATIONS

During the performance of this program methodology for laboratory and on-stream measurement of calcium, magnesium, sulfite, sulfate and H^+ concentration were reviewed, evaluated and developed. In a subordinated effort, methodology for nitrite/nitrate and carbonate were examined to permit an evaluation of direction and scoping of future work. For the instrumental techniques recommended, the alternative data acquisition and reduction systems to permit the widest range of choice in automation versus cost have been identified. The conclusions and recommendations regarding methodology provided in the following paragraphs are presumptive of the given concentration ranges and accuracy requirements as delineated by Bechtel and Radian Corporations.

For on-line slurry analysis for total calcium, magnesium, sulfur and other elements that may be of importance to the process operation and as iron, manganese, cobalt, chloride, etc., X-ray fluorescence (XRF) has been judged the best process analyzer. Extensive evaluation of available technology has led to the conclusion that, as of this writing, Applied Research Laboratories (ARL) offers the best process XRF system. Because sample pretreatment and phase separation is not required with the ARL slurry presenter, continuous, real-time readout of up to 15 separate elements can be obtained. A scanning channel is recommended for detection of trace or other compositional variations that may impact process operation.

The choice of a laboratory XRF unit is not as clear-cut as several vendors offer competitive equipment. Nonetheless, the ARL laboratory units are definitely among the best available in terms of sensitivity, versatility, and automatability. In addition, both the process and laboratory units come equipped with several optional, but most importantly, field proven data acquisition and reduction systems ranging from digital recorder output of signal to printed hardcopy of percent composition distribution utilizing sophisticated computer methodology for correction of matrix effects and automated calibration for substrate variations.

Because all other analytical techniques require rapid phase separation at the point of process sampling, on-line separation techniques were developed in the laboratory and are recommended for evaluation and adoption at

TVA. The system recommended is comprised of a cyclone centrifugal separator, such as the Demco unit tested in this study. This unit significantly decreases the solid content of the analytical effluent but does not yield an optically clear stream. Therefore, a second stage separator is necessary. With the given information is is not possible to determine if a polishing filter will suffice or if an intermediate centrifuge stage will be required. For initial field testing, the two-stage cyclone + filter separator system based on the design in Figure 7 is recommended. A high capacity, parallel dual cartridge filter unit such as the AFM-Cuno unit warrants testing for this application.

Whereas XRF can provide elemental analysis of the heterogeneous slurry as well as separated liquid and solid, the very low solubility of some species and trace concentrations of others of concern may require a more sensitive liquid phase analyzer. Atomic absorption (AA) spectrophotometry has been shown to meet this requirement in the experimentation reported in this document. At the present time, however, there are no on-line or batch flow automated instruments that can be considered process units. On the other hand, multiple lamp (element) units for very rapid and simple laboratory AA analyses are commercially available. Several units are available as dual AA/atomic emission (AE) spectrophotometers while even more versatile instruments have interchangeable flameless attachments. In selecting a laboratory AA, the trade-offs of simplicity and speed, cost and versatility must be made by the user, TVA. A list of AA instrument manufacturers recommended for consideration or for contact for requesting competitive bids was provided in Section 2.4.2.

Atomic or molecular emission techniques have been identified as exceptionally promising for the analysis of total dissolved sulfur in the aqueous phase of wet scrubber slurries. Current methodology is based on the tedious and time-consuming total oxidation to convert all sulfur species to sulfate, followed by precipitation. It is suggested that a small feasibility study be funded to determine if the aspirator-burner assembly design parameters can be optimized and fixed to eliminate variations in excitation energy. The potential range of applicability appears to fill a void in current technology for sulfur measurement and is in the range anticipated in the wet scrubbers.

Of the sulfur species in the slurry, the sulfite ($SO_3^=$) and bisulfite (HSO_3^-) S(IV) species were considered extremely important for process optimization considerations including efficiency, "scaling" and reagent regeneration. No acceptable method for the rapid, automated or on-line measurement of S(IV) species was available and consequently the UV spectrophotometric method utilizing the bleaching of the furfural UV absorption at 276 *nM* was developed. The recommended instrumental laboratory method is presented as Appendix E. A plan for complete automation of the method was developed (Section 3.4) which will permit automatic analysis of approximately 100 samples per eight-hour shift. Immediate implementation of this plan is urged to support start-up and operation schedules at TVA.

Several potentially automatable instrumental laboratory methods for sulfate species in solution were evaluated theoretically and experimentally (see Section 2.6). Based on the data generated and information from vendors and users, two methods specific for sulfate are recommended for further evaluation and development, i.e., 1) sulfate precipitation as barium sulfate with either a measurement of turbidity optically or by measurement of excess barium by AA, and 2) the ion exchange reaction with barium chloranilate and measurement of the free chloroanilic acid colorimetrically. Because these methods are either time-consuming or suffer from species interference, the technical approach required would parallel that utilized to develop the sulfite/bisulfite method to determine and eliminate interferences present in the wet scrubber environment and optimization of parameters. The sulfate could be determined by difference very rapidly and conveniently if the total sulfur analyzer is selected for development.

The feasibility of the batch automated or continuous carbonate determination by pyrolysis/acidimetric CO_2 release followed by quantitative NDIR measurement has been demonstrated experimentally. The method should be rapid, specific accurate and simple to instrument for specific candidate scrubber processes. The nitrite/nitrate methodology literature was reviewed and three candidate methods were identified and evaluated. It is not possible to select one for recommendation at this time. Further evaluation is necessary.

Finally, the bench scale wet scrubber process loop which was designed and constructed for this study was found to be exceptionally valuable in providing dynamic simulation of the process stream for methods development and evaluation. Furthermore, the system was shown to be extremely useful for understanding the wet scrubbing reaction mechanisms. For example, it was determined that for bench scale scrubbing experiments, the rate limiting step in holding tanks is that of calcium sulfite precipitation which could control the effectiveness of sulfur dioxide absorptions by wet limestone scrubbing. The unit will find utility in the development of other process analysis techniques and is sufficiently versatile to simulate most other candidate scrubbing processes.

6.0 NEW TECHNOLOGY

This section provides documentation of new methodology and technology contributions specifically beneficial to the analysis and characterization of wet scrubber processes that were developed or conceived under EPA Contract 68-02-0007.

Two of the new technology innovations were of sufficient novelty and potential use to warrant submitting invention disclosures to the TRW Patent Office. The subject matter of these disclosures are listed below:

Docket No.	Title
72-096	Wet Scrubber Bisulfite Analyzer
72-100	Total Sulfur Analyzer in Process Streams

In addition to the invention disclosures three other new innovations were identified during the program which offer unique approaches to characterization of wet limestone scrubber process streams. In addition to the invention disclosures the following new technology items are described below:

- Application of X-ray fluorescence methodology for numerous slurry elements
- Automatable solid and dissolved carbonate method
- Combined use of a small scale cyclone and dual filter separator system for continuous phase separation

6.1 WET SCRUBBER BISULFITE ANALYZER

An instrument based on bisulfite bleaching of the 276 *nM* UV absorption of furfural was conceived. This approach has been developed to be free from wet scrubber species interference, and is currently laboratory operational with elapsed analysis time for each sample of five minutes. A plan for automation to allow approximately 100 analyses per eight-hour shift with little operator involvement was proposed and is discussed in Section 3.4.

6.2 TOTAL SULFUR ANALYZER FOR PROCESS STREAMS

A new conceptual technique for determining sulfur in solution or dissolved from the solid phase based upon atomic emission or molecular emission utilizing flame, microwave and other suitable excitation was generated during this program. The sulfur analysis range, believed to fill the current void in the state of the art from the low ppm level to 10 *mM*, is directly applicable to the wet scrubber slurry and is adaptable to dissolution of slurry solids. The method possesses the potential simplicity accuracy and cost effectiveness of the widely accepted AA technique.

6.3 X-RAY FLUORESCENCE ANALYSIS OF ELEMENTS

The utility of the X-ray fluorescence technique was demonstrated for application to all wet scrubber samples. The state of the art of this analytical technique for automated laboratory and continuous on-line analysis permits analysis of calcium, magnesium and most other elements possibly of importance to scrubber operation. Total sulfur can be determined quantitatively above approximately 0.03% absolute. The decided advantage to the wet scrubbing program is accuracy, simplicity and cost effectiveness on this single versatile analytical tool. Utilizing the recommended ARL equipment, up to nine slurry streams can be analyzed for up to 15 elements of a simultaneous and continuous basis with no sample pretreatment. The technique is effective for the two-phase slurry or separated liquor and/or solids.

6.4 PYROLYSIS/ACIDIMETRIC CARBONATE METHOD

Experimentation with actual and simulated scrubber solids and liquor was performed in this study, utilizing pyrolysis for solids and acidification for liquids to liberate carbon dioxide. In the preliminary tests, quantitative detection was accomplished by ebulliometry and gravimetry, however, an automated instrumental method has been proposed with non-dispersive infrared as the primary detection candidate and gas chromatography as a reasonable back-up detector. The range of applicability is extemely wide.

6.5 CONTINUOUS SLURRY PHASE SEPARATOR

A continuous staged separation system has been designed which is capable of achieving "instantaneous quenching" of liquid/solid reaction in less than 15-30 seconds. The system which provides an optically clear liquor stream for continuous analysis or grab sampling, is comprised of a miniature cyclone centrifugal separator from DEMCO and a downstream dual-parallel polishing filter unit. The current design calls for minimum slurry feed of one gallon/min and is easily incorporated in a self-contained portable cart.

APPENDIX A

SURVEY OF STANDARD ANALYTICAL METHODS FOR SLURRY COMPONENTS

This appendix delineates wet and some standard instrumental methods for 16 of the key chemical species potentially present in limestone slurries. Tabulated are the components to be measured, the principles of the method, potential interferences and related comments. In general, utilization of these methods requires separation of the phase prior to analysis.

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TABLE A.I

SURVEY OF STANDARD ANALYTICAL METHODS FOR SLURRY CONSTITUENTS

Components	Reference Techniques	Method	Interferences	Comments	References
SO_2	West-Gaeke Titrimetric(H_2O_2) Turbidimetric Iodometric	Colorimetric(560mμ) automated	Ozone + NO_2 should be $<SO_2$	Absorb in sodium tetrachloromercurate add pararosaniline + formaldehyde. Sensitivity 0.005 to 5 ppm.	18, 19, 20, 21
SO_3	Iodometric		Reducing agents		18, 19, 20, 21
NO_x	Saltzman(NO_2)	Colorimetric (550mμ automated for NO and NO_2 ($KMnO_4$ + NO → NO_2	5/1 ozone/NO_2 small interference. 30/1 SO_2/NO_2 slow bleaching	Sulfanilic acid + N(1-naphthyl)-ethylenediamine dihychrochloride and sodium nitrite. Sensitivity ppb to 5 ppm.	21
NO_3^-	Brucine	Colorimetric(470mμ)	NO_2^-		22
	Colorimetric	2,4 phenoldisulfonic acid (480 mμ)	Remove Cl^- with Ag_2SO_4		
NO_2^-	Colorimetric	(520mμ) diazotize-sulfanilic acid 1-naphthylamine	Heavy metals		22
$SO_3^=$	Iodometric	I_2-titr. excess with $Na_2S_2O_3$ (or arsenite)	Reducing species		18, 23
$SO_4^=$	Turbidimetric	As $BaSO_4$	$CO_3^=$	Fair precision ≥ 8 mg	18, 24
	Titrimetric	Add $BaCl_2$ and indicator			
HSO_3^-	Quarternary ammonium salt	Titr. with perchloric acid	$SO_3^=$		18, 25, 26
	A.C. polarographic				
	Colorimetric and U.V. spectrophotometric				

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
$CO_3^=$	Gravimetric	CO_2 on ascarite		Also manometric	28, 29
	UV spectrometric				
HCO_3^-	Gravimetric	CO_2 on ascarite		Also manometric	28
$\left.\begin{matrix} CO_3^= \\ HCO_3^- \end{matrix}\right\}$	Titrimetric	Sr^{++} titr. each ion separately			4
Cl^-	Turbidimetric	$AgNO_3 \rightarrow AgCl$(560mμ)		Nephelometric even more sensitive. Very sensitive $5x10^{-4}$N in Cl and above	28
	Titrimetric	$AgNO_3$ + dye for end pt.			
Ca^{++}	Gravimetric	(NH_4) MoO_4 weigh as Ca MoO_4	Many sepn. nec.	Good separation from Mg.	28, 30
	Volumetric	Dissolve CaO_x in dil. H_2SO_4 and titr. with $KMnO_4$			
	EDTA		Mg interferences		
	Flame emission				
	Atomic absorption				
Mg^{++}	EDTA-Volumetric	Erichrome Black-T indicator (pH 10)	Ca interferences	Also a colorimetric technique.	26, 30
	Gravimetric	ppt. with $(NH_4)_2$ HPO_4	Separate Ca as $CaMoO_4$		
	Atomic absorption				
K^+	Gravimetric	ppt. as $KClO_4$ or K_2PtCl_6			31
	Flame Emission	(767 mμ)	"Use "radiation" buffers		
Na^+	Gravimetric			Lengthy	31

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
	Flame Emission	(589mμ)	Use "radiation" buffers		
Fe^{++}	Titrimetric	Redox- Ce^{++++} in acid soln. or $KMnO_4$ or $K_2Cr_2O_7$	Many metals	Or oxid. to Fe^{+++} and use colorimetric, EDTA, etc.	26, 32
Fe^{+++}	Titrimetric	Redox- in acid + NH_4SCN titr. with std. $TiCl_3$ or $Ti_2(SO_4)_3$	Many metals	Sepn. nec.	26, 30, 32
	Colorimetric	1,10-phenanthroline + $NH_4OH\cdot HCl$ (or hydroquinone)			
	EDTA				
	Atomic absorption				
Mn^{++}	Colorimetric	(540mμ) oxid. with KIO_4 in H_2SO_4 to MnO_4^-	Bi, Cl^-, Sn, Br, O_x, I^- NO_2^-, SO_3, and Fe(II) Ce, Cl^-, Co, Cr, F^-, HNO_2, Ni and U		32, 33
	Titrimetric	Redox-$NaBiO_3$ titr. with $KMnO_4$ or $(NH_4)_2S_2O_3$ + $AgNO_3$ titr. with AsO_2^-			
	Volhard	Volumetric-titr. with $KMnO_4$	Interferences by ppt.		
	Titrimetric	KIO_4(oxid. to MnO_4^-). $Hg(NO_3)_2$ to ppt. - add $FeSO_4$ and back titr. with $KMnO_4$			
	Atomic absorption				
Co^{++}	Volumetric	Titr. with KCN or EDTA		Sepn. nec.	26, 28, 30
	Colorimetric	Nitro-R salt-control pH	Sepn. of interferring ions		

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
	Gravimetric	Ppt. with α-nitroso-B-naphthol. Ignite and weigh as Co_3O_4			
	Atomic absorption				
V^{+++++}	Potentiometric	Oxdn. V → V(V) and titr. with $FeSO_4$ using Pt and colomel electrodes.			26, 28, 30,
	Colorimetric	Phosphotungstate method (409 mμ)	Bi, I^-, K, Mo, NH_4^+, SCN^- Sb, Sn, Ti, and Zr. Colored ions such as Co, CrO_4, Cu, etc.		
	Colorimetric	8-hydroxyquinoline and ext. with $CHCl_3$(550mμ) pH 3.5-4.5		Remove interferences by extraction of $CHCl_3$ layer with alk. (pH 9.4) aq. soln. (V to aqueous phase) then reextract V with $CHCl_3$.	
	Atomic absorption				
V^{++++}	Volumetric	Red. to V(IV) and titr. with $KMnO_4$	As, Cr, Fe, Pt, H_2S, and Sb		26, 28, 30
	Atomic absorption				
Hg^{++}	Colorimetric	Dithizone method (500 mμ) [Hg(II)dithizonate or (610 mμ) excess dithizone]			28, 30
	Volumetric		Many metals and anions		
	Gravimetric		Many metals and anions		
	Atomic absorption				

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
Al^{+++}	Gravimetric	Ppt. with 8-hydroxyquinoline		Many separations necessary	28, 33
	Volumetric	Ppt. with 8-hydroxyquinoline add excess acid and std. $KBrO_3$-KBr soln. then excess KI and titr. liberated I_2 with $Na_2S_2O_3$, starch indicator.			
	Colorimetric	Reac. with NH_4 aurintricarboxylate (525 mμ)	Cu + Ni		
	Atomic absorption				
Pb^{++}	Colorimetric	Dithizone (520 mμ) or Di-(3-naphthyl-thiocarbazone.	Other metals		26, 33
	Atomic absorption				
As^{+++}	Titrimetric	Using $KMnO_4$ as titrant			
	Colorimetric	Ammonium molybdate (840 mμ)		Other colorimetric methods.	30. 33
	Atomic absorption				

APPENDIX B

SURVEY OF ELECTROCHEMICAL METHODS FOR ANALYSIS OF DISSOLVED OXYGEN AND SULFUR DIOXIDE

This appendix summarizes electrochemical methods for the determination of dissolved oxygen and sulfur dioxide contents. Criteria used for evaluation of these methods included:

- The present state of development (laboratory technique, availability of laboratory or process stream instruments)
- Sampling mode
- Specificity and interferences
- Pretreatment of sample for analysis (concentration, filtration, adjustment of pH)
- Useful concentration range, sensitivity, accuracy, precision
- Temperature requirements
- Analysis time
- Data reduction capability
- Requirements for further development
- Maintenance requirements
- Cost
- Life time and cycle life
- Commercial instruments

Table B.I identifies electrochemical methods for the determination of oxygen and Table B.II electrochemical methods for the determination of sulfur dioxide.

TABLE B.I

ELECTROCHEMICAL METHODS FOR THE DETERMINATION OF OXYGEN

B.I.1 Direct Polarographic Determinations

The Present State of Development:	The technique is based on the measurement of diffusion current for the reduction of dissolved oxygen gas on mercury, gold or platinum electrode. The reduction on mercury is well studied. Reduction waves on solid electrodes are complicated by reduction of adsorbed oxide film when studied by scan voltammetry. Most of the work is accomplished using solid electrodes with a membrane. The membrane provides selective sampling for oxygen gas. The fine particulate suspensions in the slurry liquid may poison the solid electrodes if used directly. Because of the relatively short life of amalgam electrodes, the direct reduction method is advisable for dropping mercury electrode only. The dropping mercury electrode is used for the polarographic determination of dissolved oxygen. The technique is suitable for laboratory bench.
Sampling Mode:	Batch sampling only.
Specificity and Interferences:	Specific for oxygen in the slurry composition. Current measured between -0.3 to 0.6 V (vs. sce).
Pretreatment of Sample for Analysis:	The sample can be used directly without the adjustment of pH.
Use Concentration Range, Sensitivity Accuracy, Precision:	Can determine down to 0.5 ppm. Higher concentration limit depends upon the slurry extract composition. Can go up to 100 ppm. The technique is capable of providing better than 5% precision at the lowest limit.
Temperature Requirements:	Can be operated at any temperature. Should be calibrated accordingly.
Analysis Time:	As the gas is reduced directly from the solution, response is high. Results obtained immediately.
Data Reduction Capability:	Current readings should be converted to concentration by analog procedure. The current should always be measured at the same time, e.g., at the end of drop life.
Requirements for Further Development:	Very little.
Maintenance Requirements:	Mercury electrode should be carefully maintained.
Cost:	Inexpensive.
Life Time and Cycle Life:	Mercury reservoir should be continuously replenished.

TABLE B.I (CONTINUED)

B.I.2 Polarographic Determination Through Membrane

The Present State of Development:	The basic principle is the same as in A.I.1. The electrode is a solid, planar electrode and is separated from the solution by a membrane through which oxygen diffuses. The solid electrode is polarized at the diffusion region for the oxygen gas. The electrode could be polarized with an external source or by a galvanic couple like lead-silver system. Lead electrode is the anode in the basic electrolyte system contained inside the assembly. The limiting diffusion current for oxygen reduction is due to the membrane permeability to oxygen. It is assumed that steady state is attained for dissolved oxygen on the sample side of the membrane. Many process instruments based on the above principle are available in the market. The technique is fairly well developed.
Sampling Mode:	Either continuous or batch.
Specificity and Interferences:	Membrane provides selectivity for oxygen.
Pretreatment of Sample for Analysis:	To prolong the life of the membrane it is better to minimize slurry particles in the sample.
Use Concentration Range, Sensitivity Accuracy, Precision:	0-40 ppm dissolved oxygen. Quite sensitive.
Temperature Requirements:	Operates from 32°F - 110°F.
Analysis Time:	Fast response, usually 30 seconds.
Data Reduction Capability:	Can be read directly as ppm by weight of dissolved oxygen.
Requirements for Further Development:	Both the galvanic and potentiostatic methods are well developed and commercial instruments are available.
Maintenance Requirements:	The electrolyte inside the system should be replenished periodically. Membrane life is usually long, unless damaged by violent physical shock. Membrane can be replaced without difficulty.
Cost:	Commercial oxygen analyzers are produced in large scale. Price is competitive.
Life Time and Cycle Life:	As the system is well-sealed and there is no moving part, the detector could last from six months to two years without servicing.
Commercial Instruments:	Potentiostatic: 1) Instrumentation Laboratory, Inc., 2) Honeywell, Model S 914-21 Do-meter, 3) Yellow Springs Instruments Co., YSI Oxygen Meter, 4) Weston and Stack, Model 400, 5) Delta Scientific, Series 3210 and 6) Beckman Instruments, Inc., Model 735. Galvanic: 1) Bio Marine Industries, Model DOA 555, 2) International Sales Associates Model QM 10, and 3) New Brunswick Scientific Co., Inc.

TABLE B.I (CONTINUED)

B.I.3 Conductivity Measurements

The Present State of Development:	The technique is based on the principle that oxygen reacts with thallium metal in aqueous medium to produce soluble conducting thallium hydroxide. The conductivity increased by 35 micro mhos/cm for every ppm of oxygen. Instruments based on this principle are available for process stream.
Sampling Mode:	Sampling can be continuous.
Specificity and Interferences:	Although the principle is specific for oxygen, as the technique is based on conductivity measurement, the solution should be demineralized for analysis to provide useful sensitivity.
Pretreatment of Samples for Analysis:	Solution should be free of ions.
Use Concentration Range, Sensitivity Accuracy, Precision:	The technique is extremely sensitive to oxygen. Conductivity is measured before entering thallium tube and again after it leaves the thallium tube - 0-1000 ppb (parts for billion by weight) can be measured.
Temperature Requirements:	Temperature should be constant. It is preferred to keep it near 25°C.
Analysis Time:	Fast.
Data Reduction Capability:	Conductivity difference is directly read as parts per billion.
Requirements for Further Development:	This method is useful for relatively pure systems, like demineralizing plants. For slurry studies, further development needed.
Maintenance Requirements:	Ion-exchange column and thallium column should be attended to periodically.
Cost:	Relatively expensive.
Life Time and Cycle Life:	The ion exchange column and the thallium column should be charged periodically or the ion-exchange column should be recycled.
Commercial Instruments:	Beckman Instruments, Inc., OA-5K DO Analyzer.

TABLE B.I (CONTINUED)

B.I.4 Coulometric Determination

The Present State of Development:	The method is based on the principle that oxygen is quantitatively reduced by electrogenerated free radicals like methyl viologen cation radical. Though the method is more suited for gaseous stream, it can be used for dissolved oxygen by batch process. A known amount of sample is added to a solution containing totally reduced methyl viologen. The reoxidized methyl viologen, is reduced by passing current, and the charge passed is equivalent to oxygen added to the sample.
Sampling Mode:	Batch sampling.
Specificity and Interferences:	Non-specific for oxygen; any oxidant will give the same result.
Pretreatment of Sample for Analysis:	Slurry solution does not need any special treatment. pH should be near 7.
Use Concentration Range, Sensitivity, Accuracy, Precision:	Not known yet. Should be in sub ppm level. Very high concentrations can be determined.
Temperature Requirements:	Any temperature.
Analysis Time:	Time of electrolysis. Would be 5-10 minutes depending on current.
Data Reduction Capability:	Directly convertible to concentration.
Requirements for Further Development:	Needs further study.
Maintenance Requirements:	Maintenance is simple.
Cost:	Inexpensive.
Life Time and Cycle Life:	Methyl viologen solution may have to be replaced after every 20 analyses due to dilution and increased volume.

TABLE B.I (CONTINUED)

B.I.5 Corrosion Probe Method

The Present State of Development:	This method is based on the measurement of corrosion potential of aluminum electrode in the solution. The potential is measured with respect to a gold electrode, which behaves like a "quasi" reference electrode. The aluminum electrode is in contact with a wetted frit, which separates the gold electrode, immersed in distilled water. The oxygen gas is sampled from the test solution, by means of a carrier gas. The sudden variation of the potential of the couple, as a transient, is related to the concentration of oxygen. This technique is still a laboratory curiosity.
Sampling Mode:	Suitable for batch sampling.
Specificity and Interferences:	Any gas affecting aluminum corrosion will give wrong reading. SO_2 may affect readings.
Pretreatment of Sample for Analysis:	No special treatment is needed, as the carrier gas carries the dissolved gas.
Use Concentration Range, Sensitivity, Accuracy and Precision:	Sensitivity is 0.1 ppm.
Temperature Requirements:	Ambient.
Analysis Time:	4-6 minutes analysis time.
Data Reduction Capability:	Analog output.
Requirements for Further Development:	Needs a lot to be done, as the method is based on empirical approach.
Maintenance Requirements:	Maintenance is delicate, as it involves measurement of corrosion potential.
Cost:	Inexpensive.
Life Time and Cycle Life:	No information is available.

TABLE B.II

ELECTROCHEMICAL METHODS FOR THE DETERMINATION OF SULFUR DIOXIDE

B.II.1 Coulometric Determination

The Present State of Development:	This method is based on the principle that sulfur dioxide solution is oxidized by bromine or iodine, which could be electrogenerated. Exact amount of bromine or iodine is produced by anodic oxidation of bromide or iodide solution and the amount of bromine or iodine produced is coulometrically found from the total current passed. Any excess bromine or iodine generated is detected by an indicator electrode, which is used for stopping electrolysis. This technique is well developed for process stream, but only for SO_2 in gases. Using these developed instruments for continuous analysis of solutions is not practical. However, these commercial instruments can be used for sulfite analysis in aqueous solutions by batch sampling.
Sampling Mode:	Batch sampling.
Specificity and Interferences:	Other reducing agents in solution, may interact with iodine or bromine. However, the slurry does not contain any other reducing agent.
Pretreatment of Sample for Analysis:	The sample should be clear, free of particles. The solution should be acidic.
Use Concentration Range, Sensitivity Accuracy, Precision:	This technique detects sulfur dioxide from 0 to 1000 ppm range, in gases. Sensitivity in ppb.
Temperature Requirements:	Ambient conditions.
Analysis Time:	There is a lag time, as this technique needs mixing and electrolysis. Maximum time requirement is about 5 minutes.
Data Reduction Capability:	The readout is in coulombs, which is directly convertible to ppm.
Requirements for Further Development:	Very little further development.
Maintenance Requirements:	For solution analysis, the reagents get continually diluted. Solutions may have to be replaced after a set of analyses.
Cost:	Price on these instruments is competitive.
Commercial Instruments:	For gas samples: 1) process analyzers, Titrilog II, 2) Barton ITT, Model 286, 3) Phillips PW-9700, 4) Beckman Model 906, and 5) Atlas Electric, Modesl 200 and 210.

TABLE B.II (CONTINUED)

B.II.2 Polarographic Determination Through Membrane

The Present State of Development:	The method is based on the principle that sulfur dioxide can be electrooxidized on a sensing electrode, at a given applied potential between the sensing electrode (Au) and a counter electrode (PbO_2). A thin membrane, selective for SO_2, separates the sample and the sensing electrode. The limiting current is due to diffusion of SO_2 across the membrane, and is proportional to SO_2 concentration in the sample. The technique is similar to oxygen detection, except the membrane is selective to SO_2 and instead of reduction current, oxidation current is measured. One such commercial instrument is available. The device can be used for both gases and solutions. However, laboratory studies have shown that the current at the sensing electrode is dependent upon the previous history of the electrode.
Sampling Mode:	Applicable to both continuous and batch sampling.
Specificity and Interferences:	The specificity depends on the membrane selectivity for SO_2 alone, and the oxidation potential. In the slurry the interfering ions would be barred by the membrane.
Pretreatment of Sample for Analysis:	The membrane isolates the sample and the electrolyte. The sample should be free of fine suspension.
Use Concentration Range, Sensitivity Accuracy, Precision:	Concentration range 0-5000 ppm.
Temperature Requirements:	Ambient 40°F - 110°F.
Analysis Time:	Less than 2 minutes.
Data Reduction Capability:	Analog readout, so directly convertible to ppm SO_2
Requirements for Further Development:	The stability and reproducibility of the sensor electrode is not fully studied.
Maintenance Requirements:	Not known. Expected to be stable for at least three months.
Cost:	Not expensive.
Life Time and Cycle Life:	Life time of the sensor is expected to be long. This could be easily replaced.
Commercial Instrument:	Dynasciences Corporation.

TABLE B.II (CONTINUED)

B.II.3 Direct Polarographic Determination

The Present State of Development:	The principle is the same as in A.II.2 except that there is no membrane separating the sample from the indicator electrode. This is possible only in the case of the liquid samples. The limiting current in both the cases is proportional to the SO_2 concentration. The direct reduction can be accomplished either on mercury electrode or Pt electrode. However, the direct reduction method can be used only as a batch process. Direct oxidation of $SO_3^=$ on platinum electrode can be for analysis.
Sampling Mode:	Batch sampling.
Specificity and Interferences:	Can be made specific for SO_2 by potentiostating.
Pretreatment of Sample for Analysis:	The pH of the solution should be near 0.
Use Concentration Range, Sensitivity Accuracy, Precision:	Not known, but should be in the same range as in A.II.2.
Temperature Requirements:	Ambient.
Analysis Time:	Sample has to be transferred to the electrochemical cell. The cell should be ready with supporting electrolyte. Time of analysis will be about 10 minutes.
Data Reduction Capability:	Analog readout. Can be read as ppm from calibration chart.
Requirements for Further Development:	The system should be studied before employing it as a routine method.
Maintenance Requirements:	Simple.
Cost:	Inexpensive.
Life Time and Cycle Life:	Lifetime, practically infinite.

APPENDIX C

INITIAL SHAWNEE PROCESS DEMONSTRATION OPERATIONAL MODES

This appendix provides details of the initial experiments for assessment of configuration, flow rates and solid loadings planned for testing by Bechtel Corporation of the wet limestone scrubbing process for abatement of sulfur dioxide emissions from the Shawnee Power Plant, Paducah, Kentucky. These details were used to identify sample locations and sampling rate in the studies conducted during this program.

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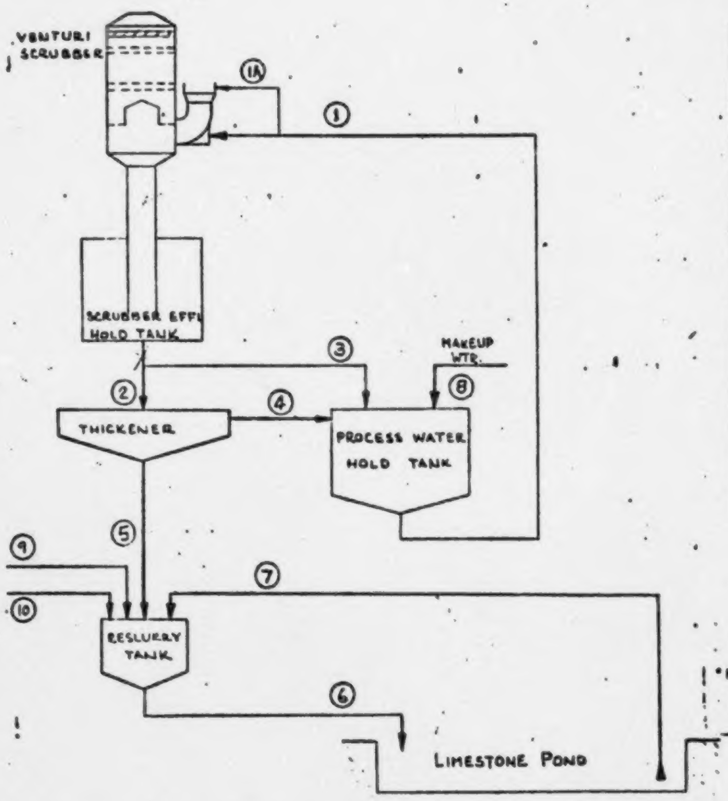
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THICKENER
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PROCESS WATER HOLD TANK
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7
RESLURRY TANK
6
LIMESTONE POND

SLURRY FLOW DATA*

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	%S	GPM	%S	GPM	%S				
1	600	14	400	5	330	0.1	30	10	5	
2	592	15	92	65	20	0.4				
3	592	15	300	65	0	0.4				
4	575	0.2	75	0.2	40	0				
5	45	30	17	30	17	10				
6	850	0.7	542	0.7	450	0.2				
7	850	0	500	0	442	0				
8	25	0	25	0	0	0				
1A	300	14	100	5	50	0.1	30	10	5	
9	8	60	8	60	4	60				FROM PLANT 200
10	45	30	17	30	17	15				FROM PLANT 800

OPERATING MODE
101

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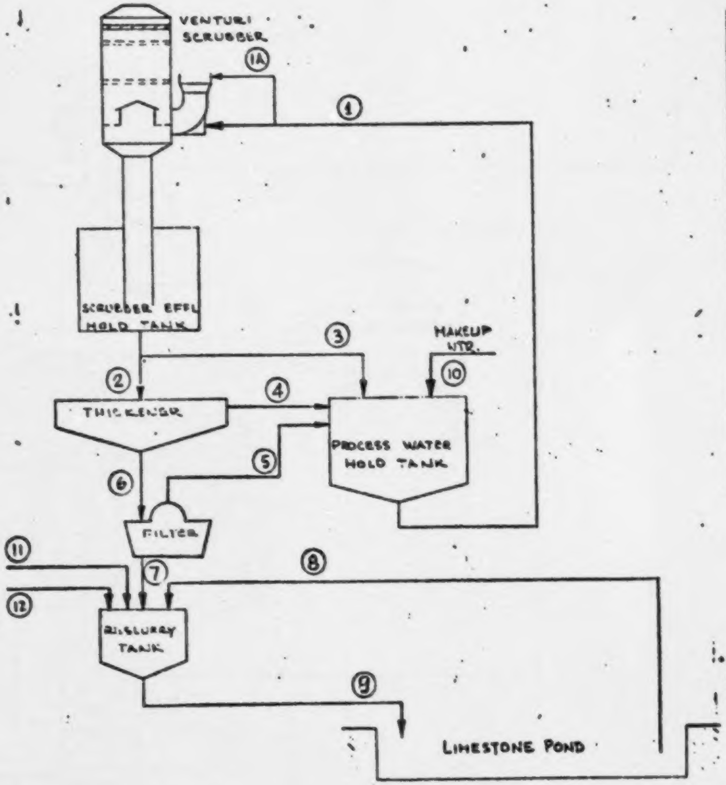
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SLURRY TANK
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LIMESTONE POND

SLURRY FLOW DATA*

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	600	14	400	5	200	0.1	30	10	5	
2	592	15	92	6.5	20	0.4				
3	572	15	300	6.5	0	0.4				
4	575	0.2	75	0.2	0	0				
5	40	0	12	0	11	0				
6	45	30	17	30	17	10				
7	6	70	5	70	2	60				
8	850	0	500	0	427	0				
9	850	0.7	530	0.7	450	0.2				
10	20	0	13	0	0	0				
1A	300	14	100	5	50	0.1	30	10	5	
11	2	60	8	60	4	60				FROM PLANT 200
12	45	30	17	30	17	15				FROM PLANT 300

OPERATING. MODE
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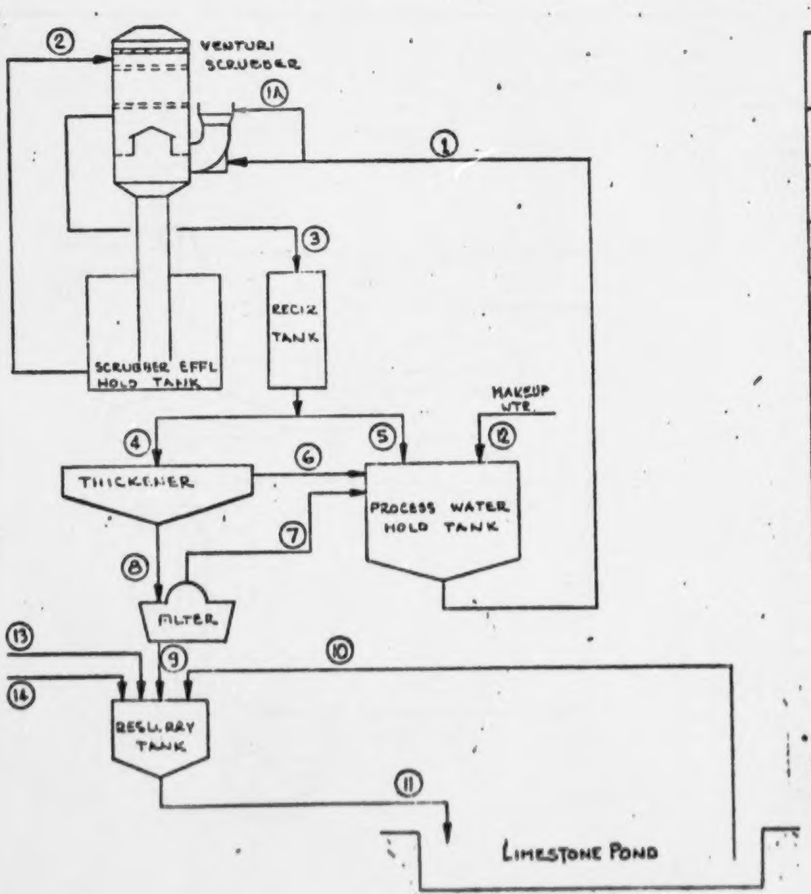
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RESLURRY TANK
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LIMESTONE POND

SLURRY FLOW DATA*

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	600	14	400	5	200	0.1	30	10	5
2	592	15	312	6.5	95	0.4			
3	592	15	312	6.5	95	0.4			
4	592	15	92	6.5	20	0.4			
5	572	15	300	6.5	0	0.4			
6	575	0.2	75	0.2	0	0.1			
7	35	0	12	0	11	0			
8	45	30	17	30	17	10			
9	6	70	5	70	2	60			
10	250	0	500	0	427	0			
11	850	0.7	530	0.7	450	0.2			
12	20	0	13	0	0	0			
1A	200	14	100	5	50	0.1	30	10	5
13	8	60	8	60	4	60			FROM PLANT 200
14	65	30	17	30	17	15			FROM PLANT 300

OPERATING MODE
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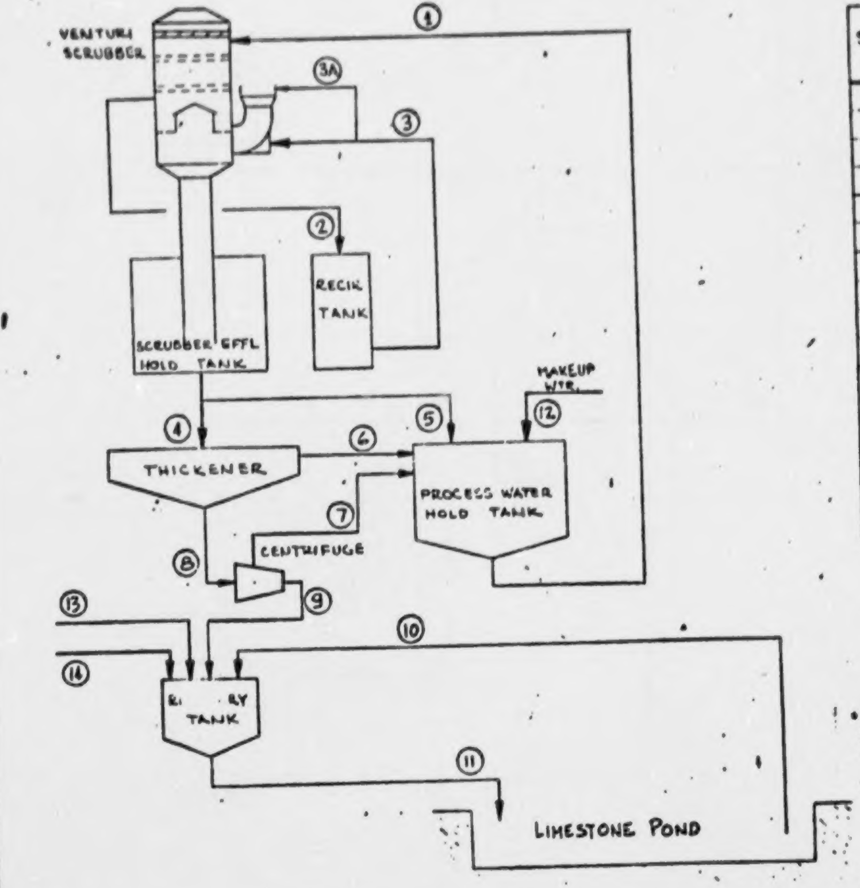
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SLURRY FLOW DATA *

STREAM No	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	%S	GPM	%S	GPM	%S			
1	600	14	400	5	230	0.1			
2	600	14	400	5	100	0.1			
3	600	14	400	5	100	0.1	30	10	5
4	592	15	72	6.5	20	0.4			
5	572	15	300	6.5	0	0.4			
6	575	0.2	75	0.2	0	0.1			
7	35	0.1	12	0.1	11	0.1			
8	45	30	17	30	17	10			
9	10	70	6	70	2	60			
10	850	0	500	0	427	0			
11	850	0.7	530	0.7	450	0.2			
12	20	0	13	0	0	0			
3A	200	14	100	5	50	0.1	30	10	5
13	45	30	17	30	17	15			
14	10	60	8	60	4	60			

FROM PLANT 200
FROM PLANT 300

OPERATING MODE
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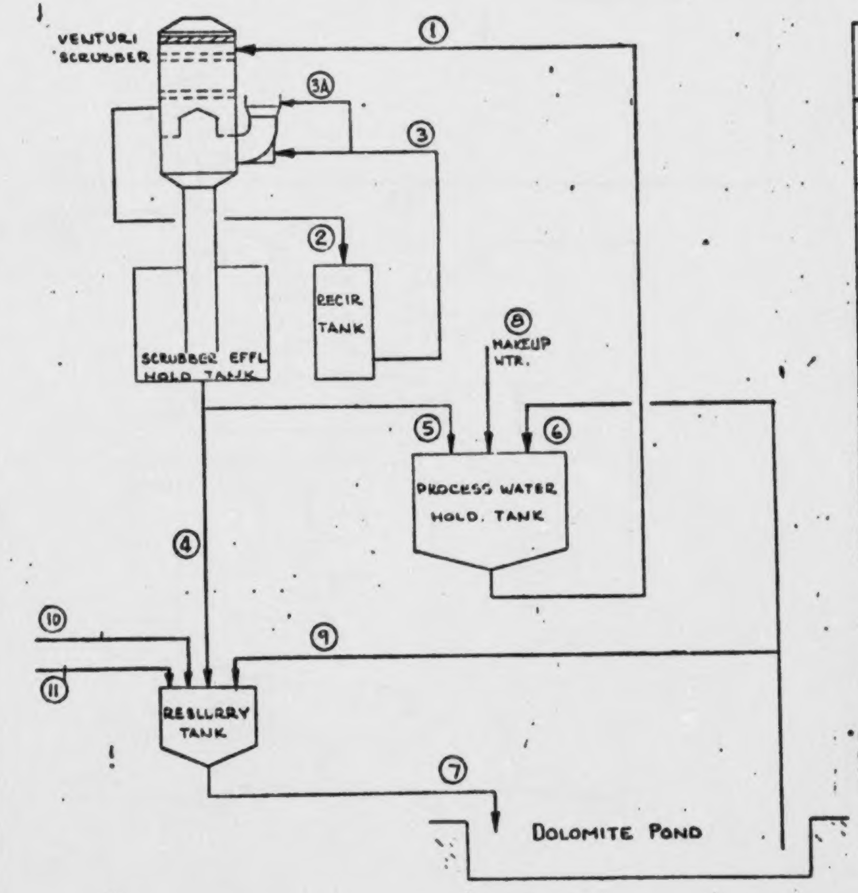
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RESLURRY TANK
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DOLOMITE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	%S	GPM	%S	GPM	%S				
1	600	0.7	400	0	400	0				
2	600	0.7	400	0	400	0				
3	600	0.7	400	0	400	0	30	10	5	
4	592	2.2	392	1.5	392	0.3				
5	200	2.2	0	1.5	0	0.3				
6	590	0	386	0	386	0				
7	612	2.2	530	1.5	450	0.3				
8	20	0	14	0	0	0				
3A	200	0.7	100	0	50	0	30	10	5	
9	260	0	122	0	50	0				
10	8	60	8	60	4	60				FROM PLANT 200
11	10	60	8	60	4	60				FROM PLANT 300

OPERATING MODE
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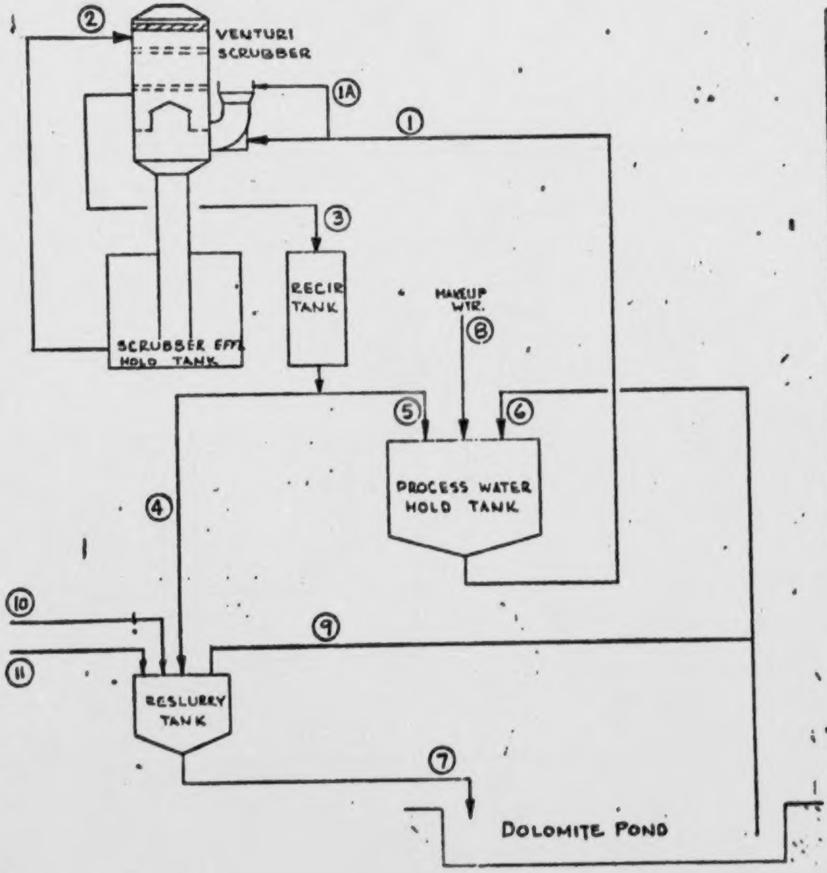
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RESLURRY TANK
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DOLOMITE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	600	0.7	400	0	400	0	30	10	5	
2	592	1.5	392	1.5	392	0.3	1			
3	592	1.5	392	1.5	312	0.3				
4	572	1.5	392	1.5	392	0.3				
5	200	1.5	0	1.5	0	0.3				
6	510	0	386	0	386	0				
7	592	1.5	530	1.5	450	0.3				
8	20	0	14	0	0	0				
1A	200	0.7	100	0	50	0	30	10	5	
9	260	0	122	0	50	0				
10	8	60	8	60	4	60				FROM PLANT 200
11	10	60	8	60	4	60				FROM PLANT 300

OPERATING MODE
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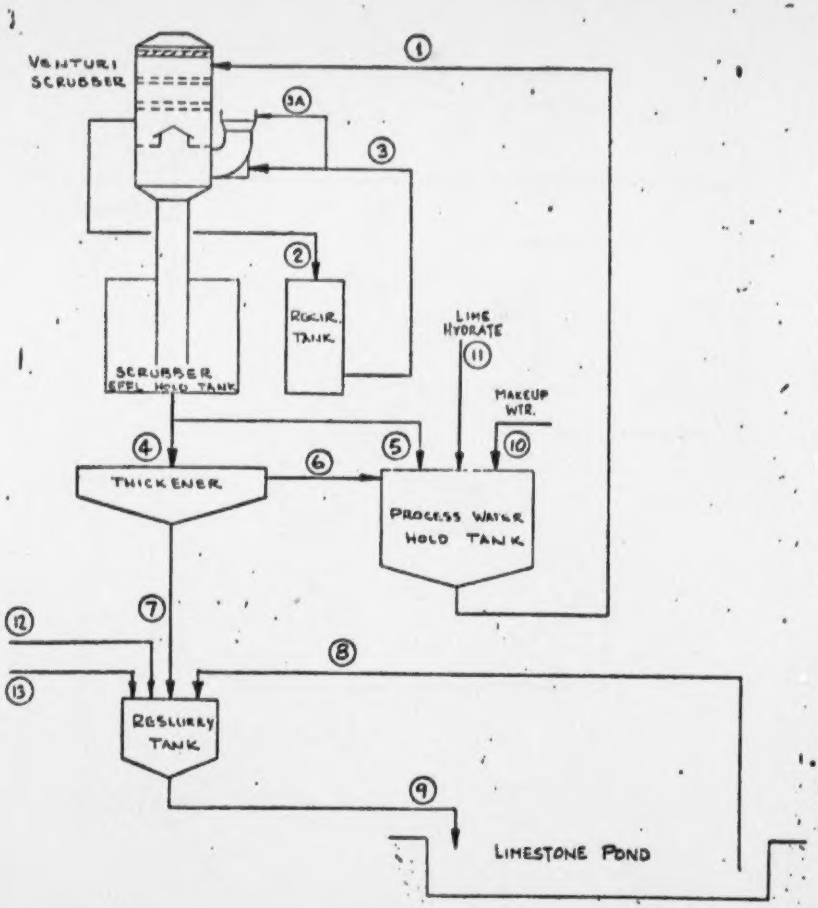
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THICKENER
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RESLURRY TANK
⑨
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	600	14	400	5	200	0.1				
2	600	14	400	5	100	0.1				
3	600	14	400	5	100	0.1	30	10	5	
4	592	15	92	6.5	20	0.4				
5	572	15	300	6.5	0	0.4				
6	572	0.2	75	0.2	0	0.1				
7	45	30	17	30	17	10				
8	850	0	500	0	425	0				
9	350	0.7	533	0.7	450	0.2				
10	25	0	25	0	0	0				
11	18 lb/MIN		12 lb/MIN		10 lb/MIN					
3A	200	14	100	5	50	0.1	30	10	5	
12	8	60	8	60	4	60				FROM PLANT 200
13	10	60	8	60	4	60				FROM PLANT 300

OPERATING MODE
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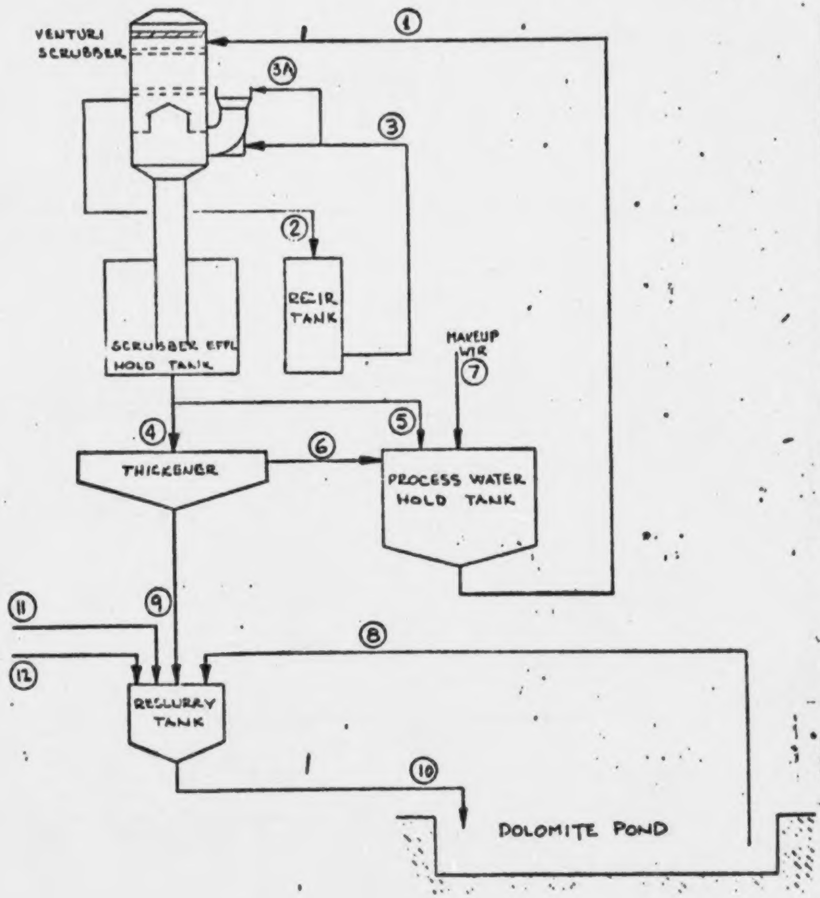
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-108-MS7	0


VENTURI SCRUBBER
①
③A
③
②
RECIR TANK
SCRUBBER EFFL HOLD TANK
MAKEUP WTR
⑦
④
⑤
⑥
THICKENER
PROCESS WATER HOLD TANK
⑪
⑨
⑧
⑫
RESLURRY TANK
⑩
DOLOMITE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	%S	GPM	%S	GPM	%S			
1	600	14	400	5	200	0.1			
2	600	14	400	5	100	0.1			
3	600	14	400	5	100	0.1	30	10	5
4	592	15	[illegible]	6.5	20	0.4			
5	572	15	300	6.5	0	0.4			
6	575	0.2	75	0.2	0.	0.1			
7	25	0	25	0	0	0			
8	823	0	500	0	412	0			
9	45	30	17	30	17	10			
10	850	1.9	542	0.7	450	0.2			
11	8	60	8	60	4	60			FROM PLANT 200
3A	200	14	100	5	50	0.1	30	10	5
12	45	30	17	30	17	15			FROM PLANT 300

OPERATING MODE
107 A

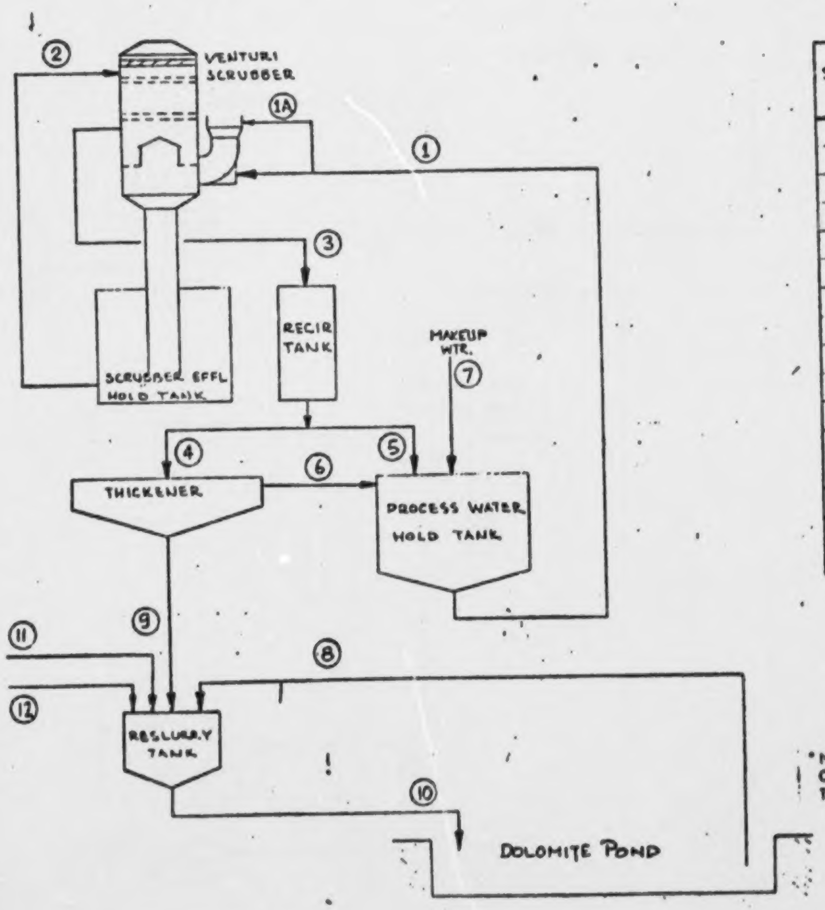
* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	9/1	GEN REV	
0		ISSUED FOR APPROVAL	FR

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET


②
VENTURI SCRUBBER
①A
①
③
RECIR TANK
SCRUBBER EFFL HOLD TANK
MAKEUP WTR.
⑦
④
⑤
⑥
THICKENER
PROCESS WATER HOLD TANK
⑨
⑪
⑧
⑫
RESLURRY TANK
⑩
DOLOMITE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	%S	GPM	%S	GPM	%S				
1	600	14	400	5	200	0.1	30	10	5	
2	592	15	392	6.5	95	0.4				
3	592	15	392	6.5	95	0.4				
4	592	15	92	6.5	20	0.4				
5	572	15	300	6.5	0	0.4				
6	575	0.2	75	0.2	0	0.1				
7	25	0	25	0	0	0				
8	833	0	500	0	412	0				
9	45	30	17	30	17	10				
10	850	1.3	542	0.7	450	0.2				
11	8	60	8	60	4	60				FROM PLANT 200
1A	200	14	100	5	50	0.1	30	10	5	
12	45	30	17	30	17	15				FROM PLANT 300

OPERATING MODE
107 B

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	3/13	GEN REV
0		ISSUED FOR APPROVAL

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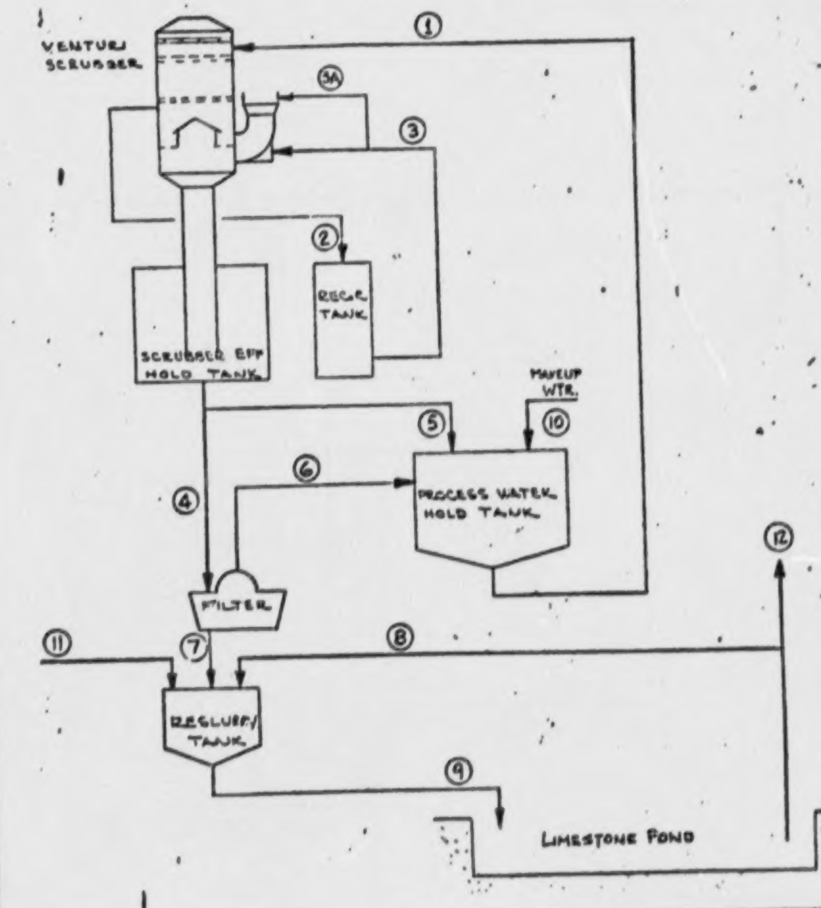
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET

6955 | M-108-MS-9 | 0


VENTURI SCRUBBER
1
3A
3
2
RECIR TANK
SCRUBBER EFF HOLD TANK
MAKEUP WTR.
10
5
6
PROCESS WATER HOLD TANK
4
FILTER
12
11
7
8
RESLURRY TANK
9
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	600	14	400	10	200	3				
2	600	14	400	10	100	3				
3	600	14	400	10	100	3	30	10	5	
4	50	15	56	11	25	4				
5	575	15	342	11	25	4				
6	42	0	42	0	20	0				
7	.15	60	8	60	3	40				
8	850	0	200	0	152	0				
9	850	2	503	1	450	0.5				
10	20	0	16	[illegible]	8	0				
3A	300	14	100	10	50	3	30	10	5	
11	850	2	295	1.5	295	0.4				FROM PLANT 200.
12	850	0	290	0	290	0				TO PLANT 200

OPERATING MODE
108 A

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	1/72	GEN REV
0		ISSUED FOR APPROVAL

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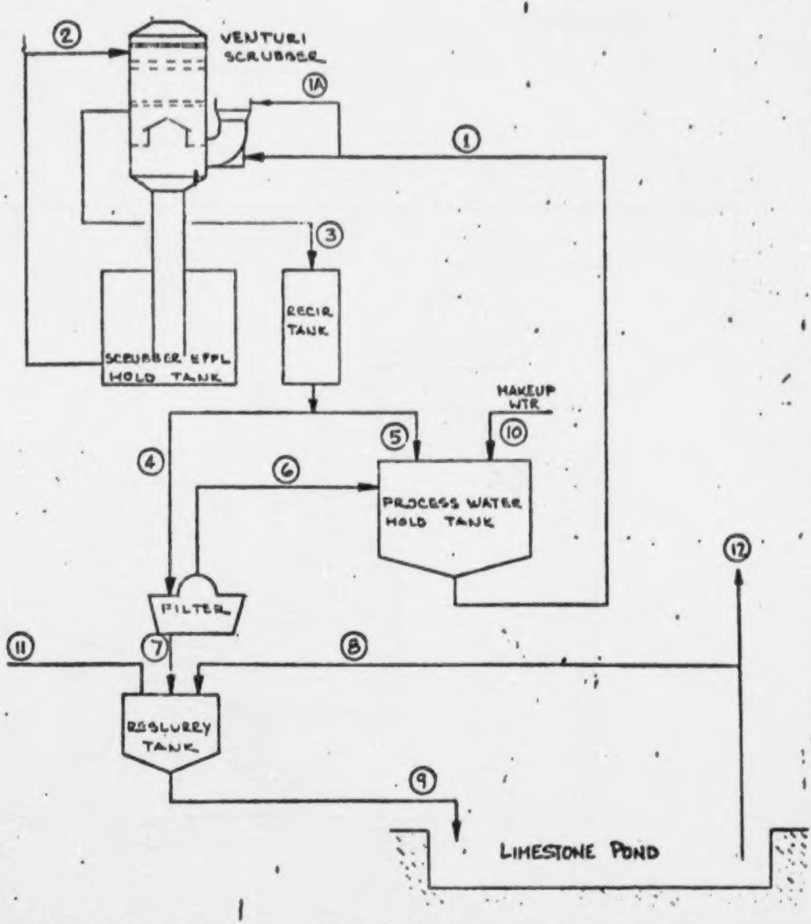
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-108 - MS-12	0



②
VENTURI SCRUBBER
1A
①
③
RECIR TANK
SCRUBBER EFFL HOLD TANK
MAKEUP WTR
⑩
⑤
④
⑥
PROCESS WATER HOLD TANK
⑫
FILTER
⑪
⑦
⑧
RESLURRY TANK
⑨
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	600	14	400	10	200	3	30	10	5	
2	592	14	392	10	100	3				
3	592	14	392	10	100	3				
4	50	15	50	11	25	4				
5	573	15	342	11	125	4				
6	42	0	42	0	70	0				
7	15	60	8	60	3	40				
8	250	0	200	0	152	0.5				
9	250	1	503	1	450	0.5				
10	20	0	16	0	8	0				
1A	300	14	100	10	50	3	30	10	5	
11	250	2	295	2.5	295	0.4				FROM PLANT 200
12	250	0	290	0	290	0				TO PLANT 200

OPERATING MODE
108 B

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

△			
△	1/72	GEN REV	
△		ISSUED FOR APPROVAL	

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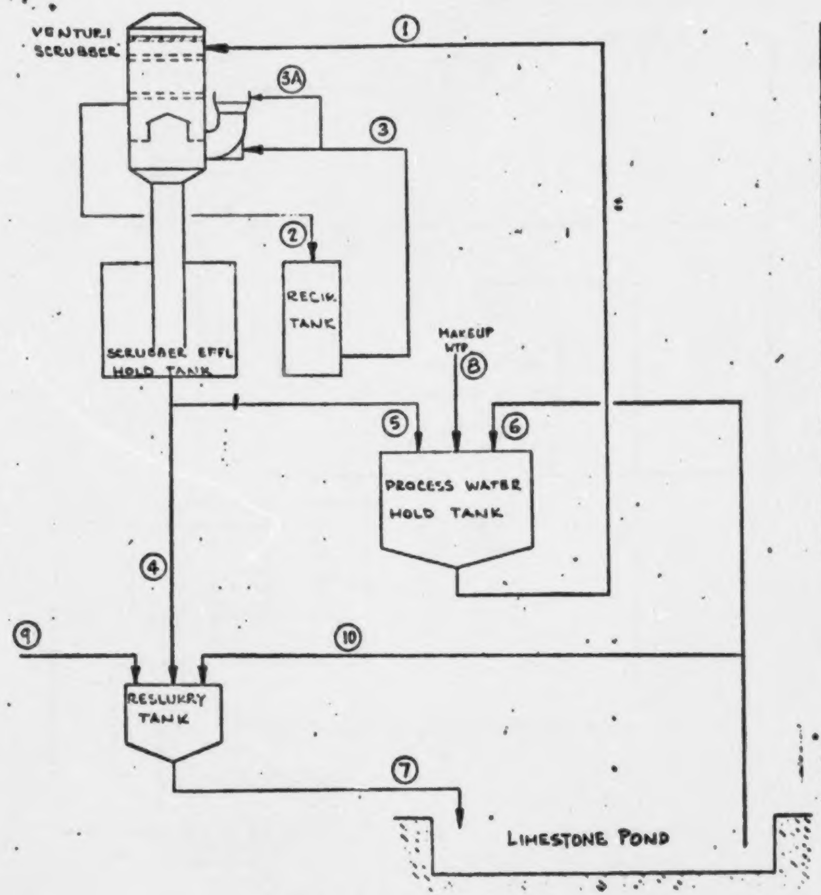
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-108-MS-13	C


VENTURI SCRUBBER
①
③A
③
②
RECIR. TANK
SCRUBBER EFFL HOLD TANK
MAKEUP WTR
⑧
⑤
⑥
PROCESS WATER HOLD TANK
④
⑨
⑩
RESLURRY TANK
⑦
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	600	0.7	400	0	400	0			
2	600	0.7	400	0	400	0			
3	600	0.7	400	0	400	0	30	10	5
4	592	2.2	392	1.5	392	0.3			
5	200	2.2	0	1.5	0	0.3			
6	575	0	386	0	386	0			
7	592	2.2	530	1.5	450	0.3			
8	20	0	14	0	0	0			
3A	200	0.7	100	0	50	0	30	10	5
9	10	60	8	60	4	60			
10	850	0	130	0	54	0			

FROM PLANT 300

OPERATING MODE
109 A

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	3/71	GEN REV
0		ISSUED FOR APPROVAL

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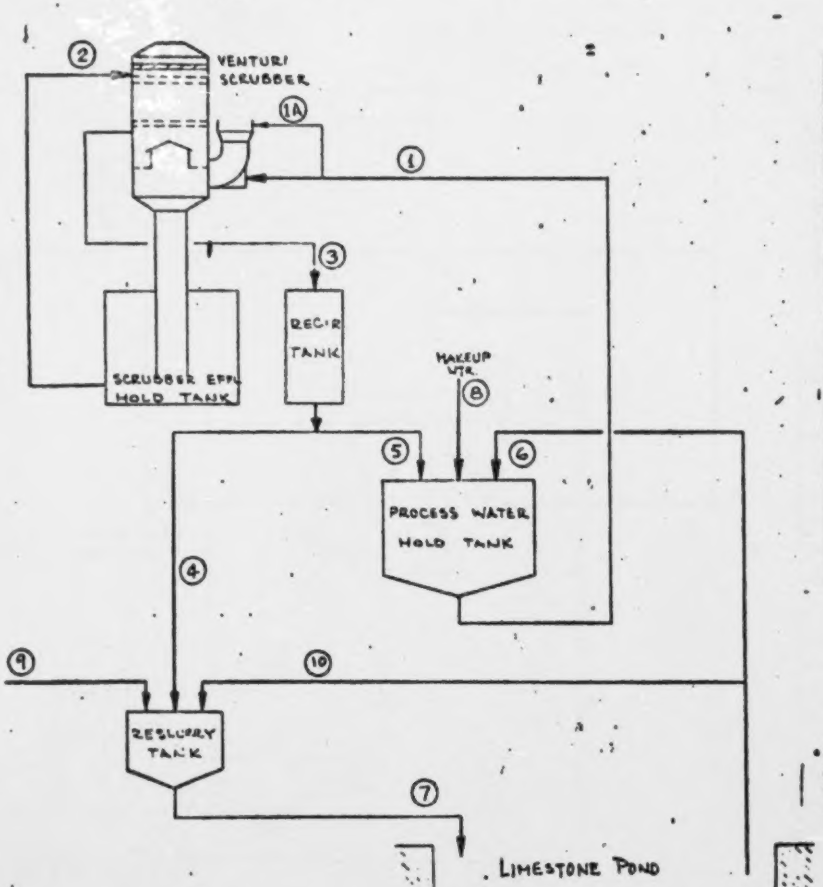
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-108-MS-10	0


②
VENTURI SCRUBBER
①A
①
③
SCRUBBER EFFL HOLD TANK
RECIR TANK
MAKEUP WTR.
⑧
⑤
⑥
PROCESS WATER HOLD TANK
④
⑨
⑩
RESLURRY TANK
⑦
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	600	0.7	400	0	400	0	30	10	5
2	592	1.5	392	1.5	392	0.3			
3	592	1.5	392	1.5	392	0.3			
4	592	1.5	392	1.5	392	0.3			
5	200	1.5	0	1.5	0	0.3			
6	590	0	386	0	386	0			
7	592	1.5	530	1.5	450	0.3			
8	20	0	14	0	0	0			
1A	200	0.7	100	0	50	0	30	10	5
9	10	60	8	60	4	60			
10	850	0	130	0	54	0			

FROM PLANT 300.

OPERATING MODE
109 B

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

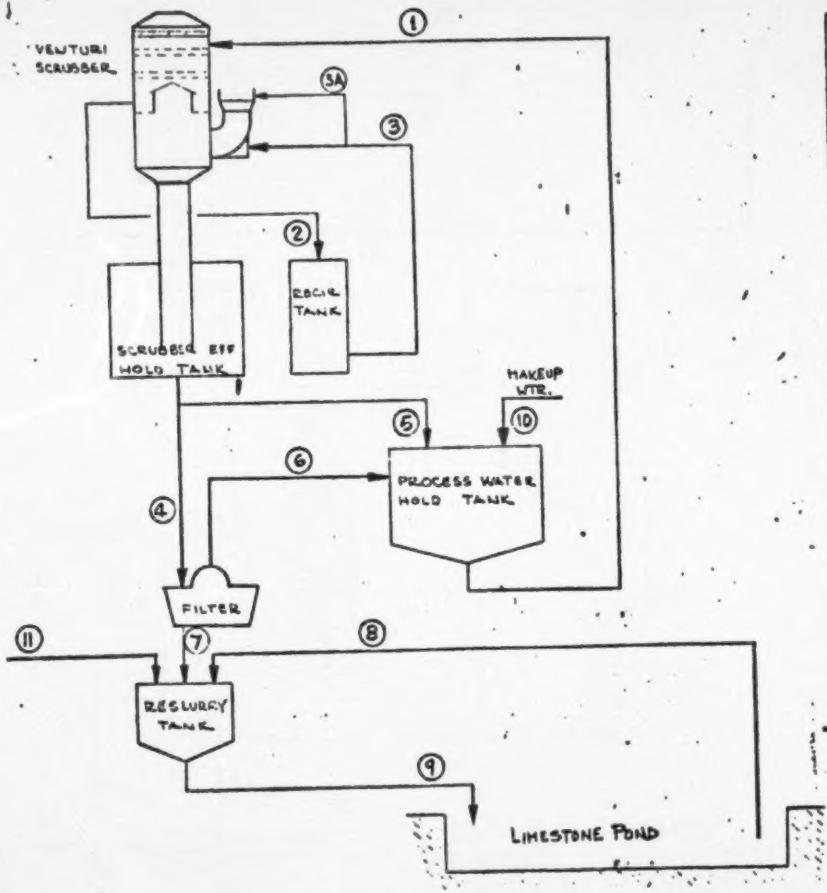
GEN REV
ISSUED FOR APPROVAL

BECHTEL
SAN FRANCISCO

N.A.P.C.A
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET

6955
M-108-MS-11
0


VENTURI SCRUBBER
①
③
③A
②
RECIR TANK
SCRUBBER EFF HOLD TANK
⑤
MAKEUP WTR.
⑩
PROCESS WATER HOLD TANK
⑥
④
FILTER
⑪
⑦
⑧
RESLURRY TANK
⑨
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	600	14	400	10	200	3			
2	600	14	400	10	100	3			
3	600	14	400	10	100	3	30	10	5
4	50	15	50	11	25	4			
5	575	15	342	11	125	4			
6	42	0	42	0	20	0			
7	15	60	8	60	3	40			
8	850	0	500	0	443	0			
9	850	2	533	1	450	0.5			
10	20	0	16	0	8	0			
3A	300	14	100	10	50	3	30	10	5
11	25	28	25	28	4	28			

FROM PLANT 200

OPERATING MODE
110A

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	5/72	GEN REV	
0		ISSUED FOR APPROVAL	

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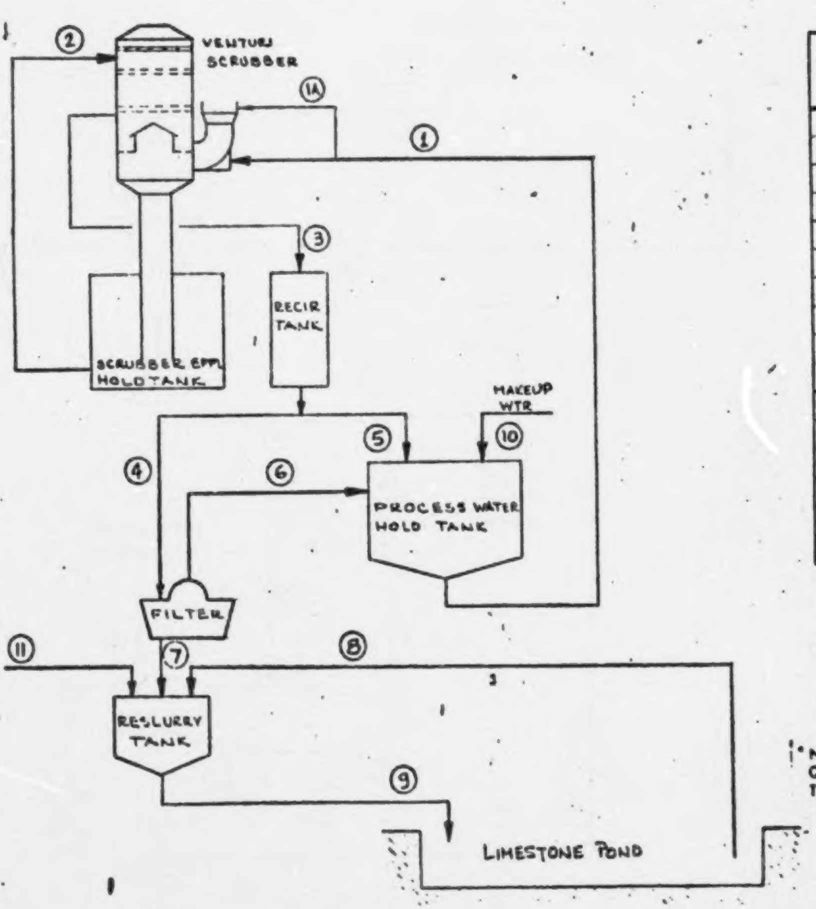
N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET

6955
M-108-MS-14


②
VENTURI SCRUBBER
1A
①
③
SCRUBBER EFFL HOLDTANK
RECIR TANK
MAKEUP WTR
⑤
⑩
④
⑥
PROCESS WATER HOLD TANK
FILTER
⑪
⑦
⑧
RESLURRY TANK
⑨
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	%S	GPM	%S	GPM	%S			
1	600	14	400	10	200	3	30	10	5
2	592	14	392	10	100	3			
3	592	14	392	10	100	3			
4	50	15	50	11	25	4			
5	575	15	342	11	125	4			
6	42	0	42	0	20	0			
7	15	60	8	60	3	40			
8	550	0	500	0	443	0			
9	550	1	533	1	450	0.5			
10	20	0	16	0	8	0			
1A	300	14	100	10	50	3	30	10	5
11	25	28	25	28	4	28			

FROM PLANT 200

OPERATING MODE
110 B

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

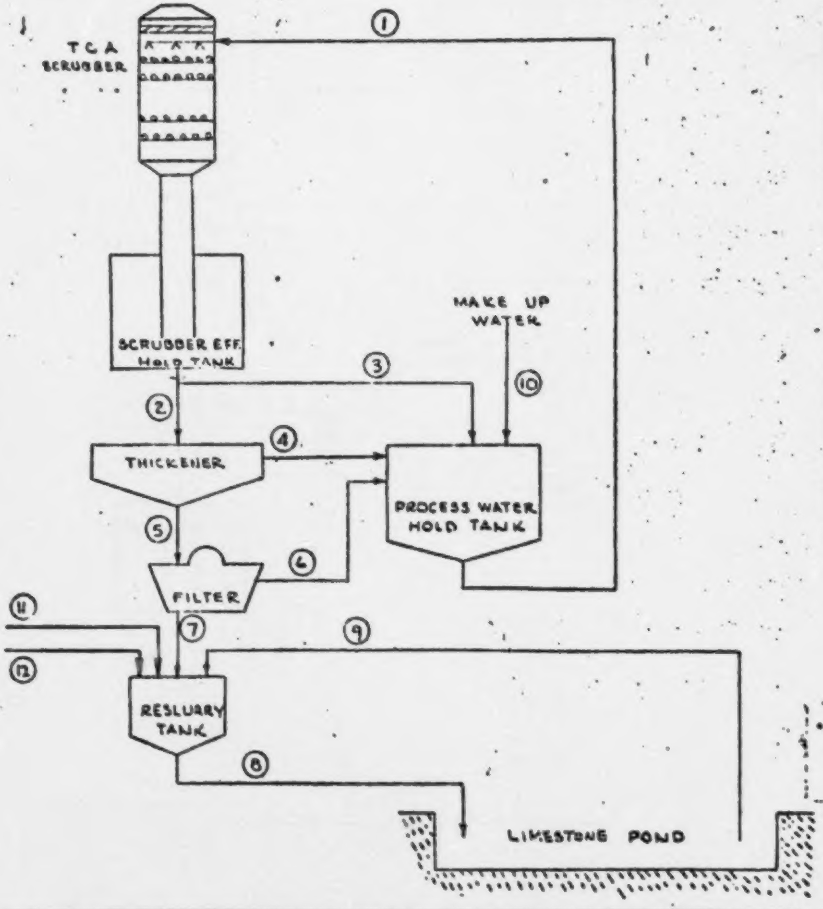
⚠					
4	5/11	GAN REV			
4		ISSUED FOR APPROVAL	[illegible]	[illegible]	[illegible]

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

VENTURI SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-108 - M8-15	0


T.C.A SCRUBBER
①
SCRUBBER EFF. HOLD TANK
②
③
MAKE UP WATER
⑩
THICKENER
④
PROCESS WATER HOLD TANK
⑤
⑥
FILTER
⑦
⑪
⑫
⑨
RESLURRY TANK
⑧
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN		MAX.	NORM.	MIN.	
	GPM	%S	GPM	%S	GPM	%S				
1	1400	15	[illegible]	5	300	0	5	5	0.5	
2	[illegible]	15	14	5	41	[illegible]				
3	[illegible]	15	[illegible]	5	0	–				
4	1375	0	123	5	20	–				
5	45	30	17	30	17	15				
6	42	0	9	0	8	0				
7	8	60	8	60	4	60				
8	850	0.8	542	0.6	450	[illegible]				
9	850	0	500	0	412	0				
10	20	0	16	0	7	0				
11	45	30	17	30	17	10				FROM PLANT 100
12	45	30	17	30	17	15				FROM PLANT 300

OPERATING MODE
201

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

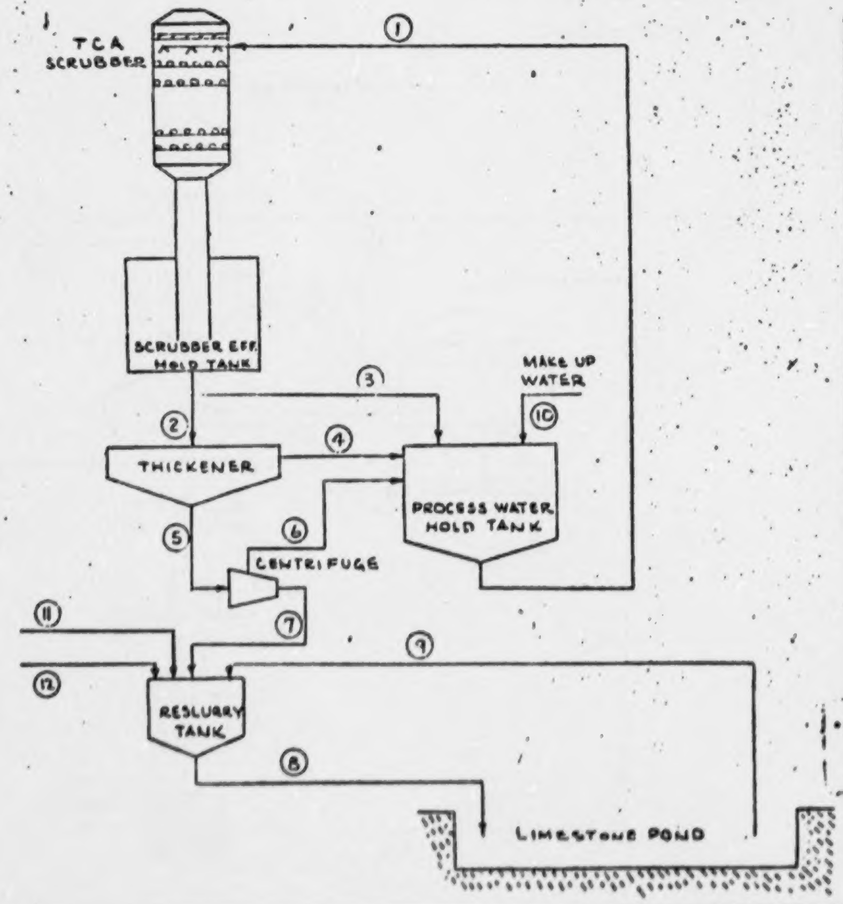
△		
1	5/72	GEN REV
△		ISSUED FOR APPROVAL

BECHTEL
SAN FRANCISCO

N. A. P. C. A.
ALKALI SCRUBBING TEST FACILITY

T.C.A SCRUBBING SYSTEM
SLURRY FLOW SHEET

6955
M-109-MS-1
0


TCA SCRUBBER
①
SCRUBBER EFF. HOLD TANK
②
③
④
MAKE UP WATER
⑩
THICKENER
PROCESS WATER HOLD TANK
⑤
⑥
CENTRIFUGE
⑦
⑪
⑫
⑨
RESLURRY TANK
⑧
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	%S	GPM	%S	GPM	%S			
1	1800	15	1400	5	[illegible]	0	5	5	0.5
2	[illegible]	15	[illegible]	5	45	0.5			
3	330	[illegible]	[illegible]	5	0	-			
4	[illegible]	0	125	5	10	-			
5	45	30	17	30	17	15			
6	42	0	7	0	8	0			
7	8	60	8	60	4	60			
8	250	0.8	530	0.6	450	0.3			
9	250	0	500	0	427	0			
10	20	0	14	0	7	0			
11	6	70	5	70	2	60			
12	45	30	17	30	17	15			

From Plant 100 (stream 11)
From Plant 300 (stream 12)

OPERATING MODE
202

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

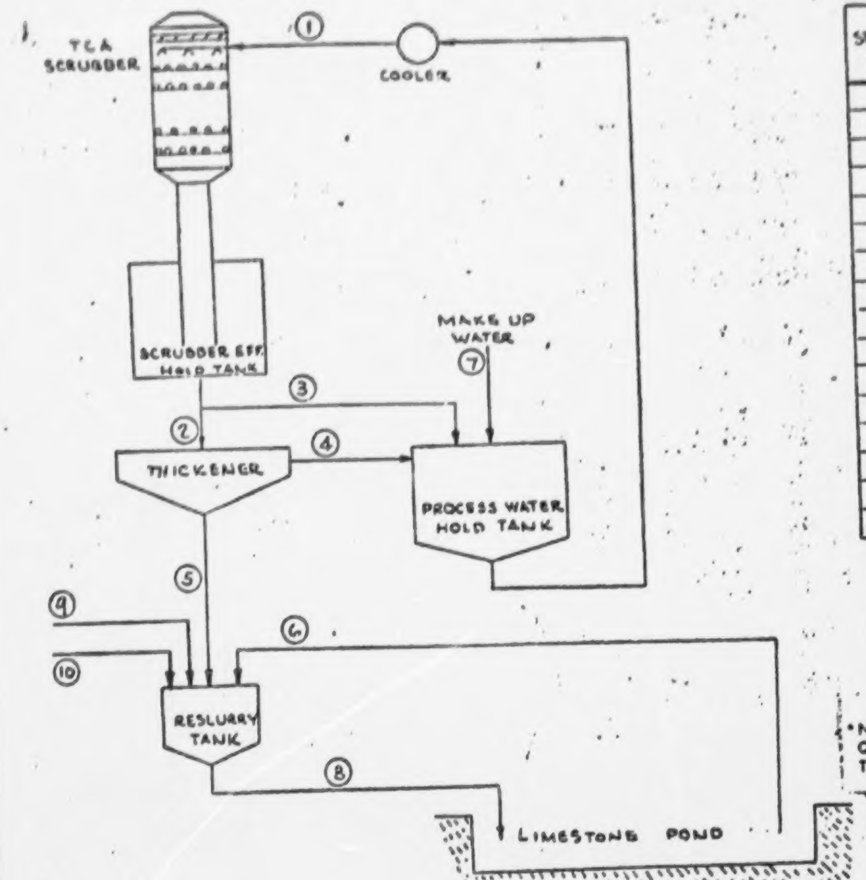
1	9/21	GEN REV
0		ISSUED FOR APPROVAL

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

T C A SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-109 - MS-2	0


TCA SCRUBBER
①
COOLER
SCRUBBER EFF. HOLD TANK
②
③
④
MAKE UP WATER
⑦
THICKENER
PROCESS WATER HOLD TANK
⑤
⑨
⑩
⑥
RESLURRY TANK
⑧
LIMESTONE POND

SLURRY FLOW DATA *

STREAM No	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	[illegible]	15	[illegible]	5	300	0	3	3	-0.2	[illegible] COOLER [illegible]
2	[illegible]	15	[illegible]	15	45	0.5				
3	1850	15	[illegible]	5	0	-				
4	1375	0	123	5	10					
5	45	30	17	30	11	15				
6	825	0	560	0	427	0				
7	25	0	25	0	7	0				
8	850	0.3	530	[illegible]	150	0.3				
9	10	70	5	70	2	60				FROM PLANT 100
10	10	60	8	60	4	60				FROM PLANT 300

OPERATING MODE
203

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

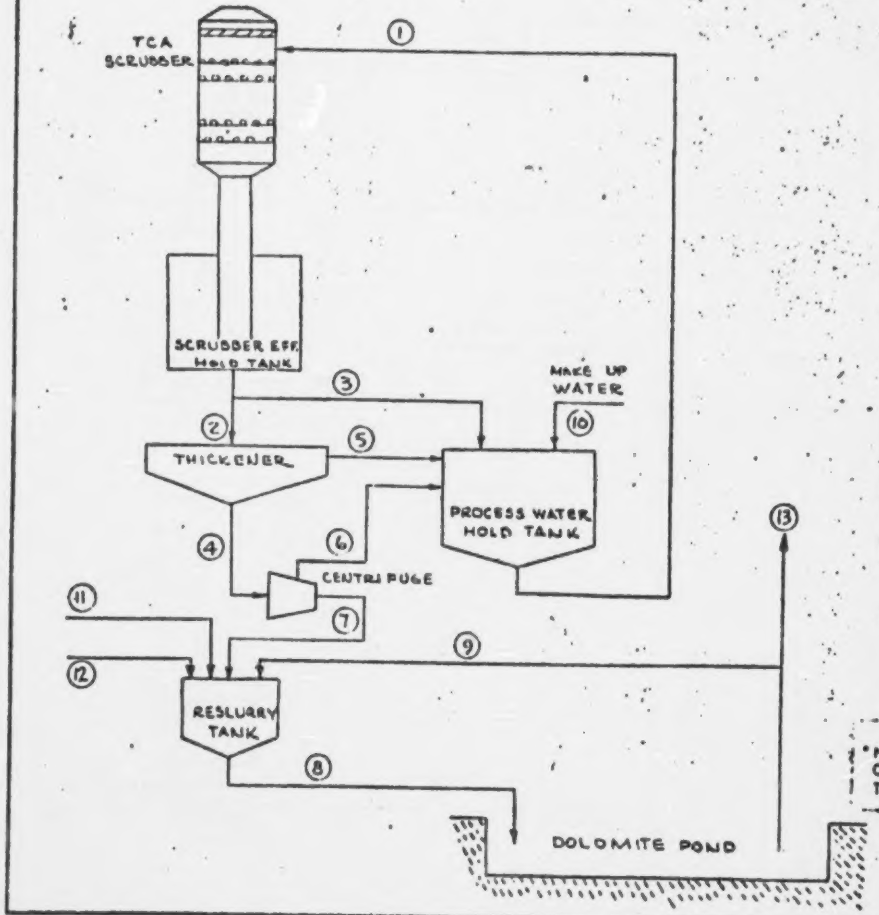
1	9/13	GEN REV	
0		ISSUED FOR APPROVAL	

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

TCA SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No	DRAWING No	REV
6955	M-109 - M3-3	0


TCA SCRUBBER
①
SCRUBBER EFF. HOLD TANK
②
③
THICKENER
⑤
MAKE UP WATER
⑩
PROCESS WATER HOLD TANK
④
⑥
CENTRIFUGE
⑦
⑪
⑫
⑨
RESLURRY TANK
⑧
⑬
DOLOMITE POND

SLURRY FLOW DATA *

STREAM №	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	1400	15	[illegible]	5	[illegible]	0	3	3	0.2
2	[illegible]	15	[illegible]	5	45	0.2			
3	1350	15	[illegible]	5	0				
4	45	30	17	30	17	15			
5	1375	0	123	5	20	–			
6	42	0	7	0	8	0			
7	[illegible]	60	8	60	4	60			
8	[illegible]	0.8	530	0.6	450	0.3			
9	260	0	122	0	50	0			
10	20	0	16	0	7	0			
11	592	2.2	392	1.5	392	0.3			FROM PLANT 100
12	10	60	8	60	4	60			FROM PLANT 300
13	590	0	386	0	386	0			TO PLANT 100

OPERATING MODE
204

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

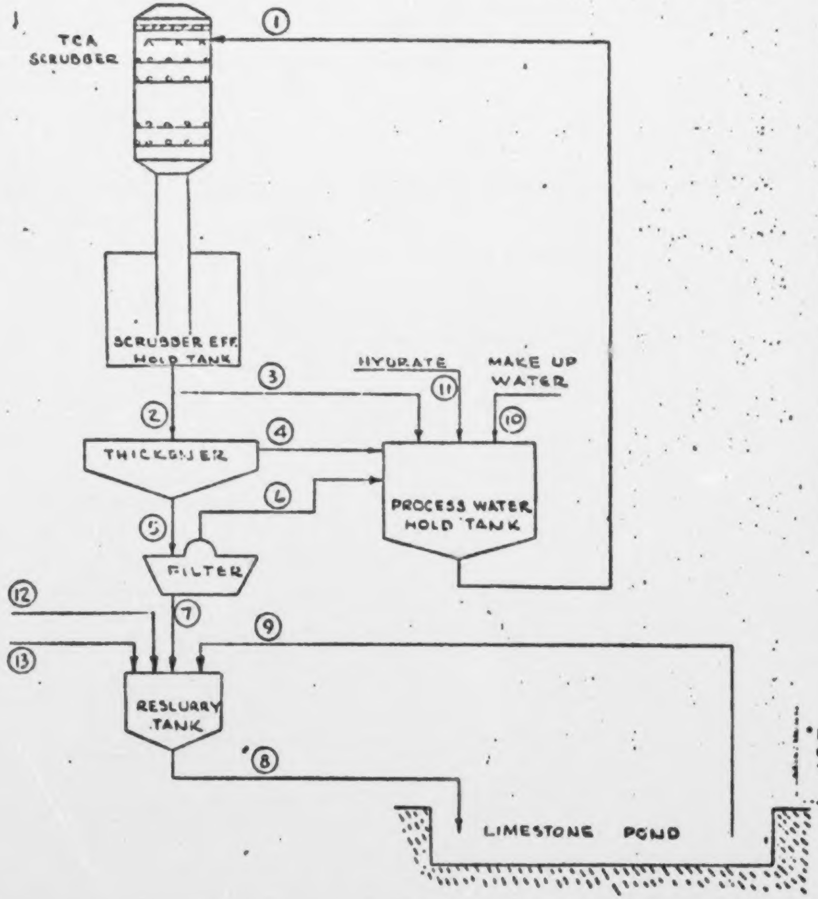
△		
4	5/11	GEN REV
△		ISSUED FOR APPROVAL

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

TCA SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-109-MS-4	0


TCA SCRUBBER
①
SCRUBBER EFF. HOLD TANK
②
③
HYDRATE
⑪
MAKE UP WATER
⑩
THICKENER
④
⑤
⑥
PROCESS WATER HOLD TANK
FILTER
⑦
⑫
⑬
⑨
RESLURRY TANK
⑧
LIMESTONE POND

SLURRY FLOW DATA *

STREAM №	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	1400	15	1400	5	300	0				
2	[illegible]	15	140	5	45	0.5				
3	350	15	[illegible]	5	0	—				
4	[illegible]	0	123	0	[illegible]	—				
5	45	30	17	30	17	15				
6	42	0	7	0	3	0				
7	8	60	8	60	4	60				
8	850	[illegible]	533	[illegible]	450	[illegible]				
9	550	0	500	0	425	0				
10	10	0	5	0	5	0				
11	30	25	11	5	10	5				
12	15	30	17	30	17	10				FROM PLANT 100
13	10	60	8	60	4	60				FROM PLANT 300

OPERATING MODE
205

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

△		
1	5/11	GEN REV
0		ISSUED FOR APPROVAL

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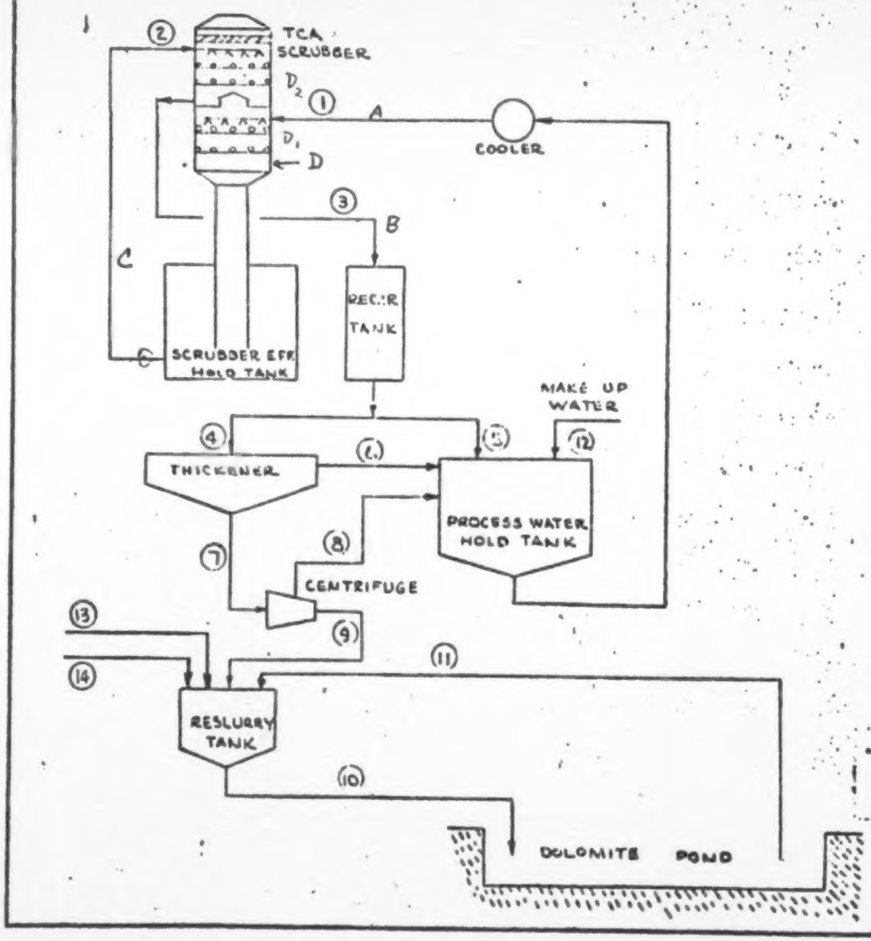
N. A. P. C. A.
ALKALI SCRUBBING TEST FACILITY

TCA SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No. 6955
DRAWING No. M-109-MS-5
REV 0


TCA SCRUBBER
②
①
D_2
D_1
A
D
C
③
B
COOLER
RECIR TANK
SCRUBBER EFF HOLD TANK
MAKE UP WATER
⑫
④
⑥
⑤
THICKENER
PROCESS WATER HOLD TANK
⑦
⑧
CENTRIFUGE
⑨
⑬
⑭
⑪
RESLURRY TANK
⑩
DOLOMITE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	1400	15	1400	5	500	0				
2	1392	15	1392	6	295	0.1				
3	1376	15	1377	6	295	0.4				
4	1392	15	72	6	30	0.1				
5	1365	15	1300	6	0	–				
6	1875	0.1	75	6	0	–				
7	45	30	17	30	17	15				
8	47	0	9	0	8	0				
9	8	60	8	60	4	60				
10	850	0.5	542	21	450	0.2				
11	850	0	500	0	412	0				
12	20	0	16	0	7	0				
13	45	30	17	30	17	10					FROM PLANT 100
14	45	30	17	30	17	15					FROM PLANT 200

OPERATING MODE
206

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	3/10	GEN REV
0		ISSUED FOR APPROVAL

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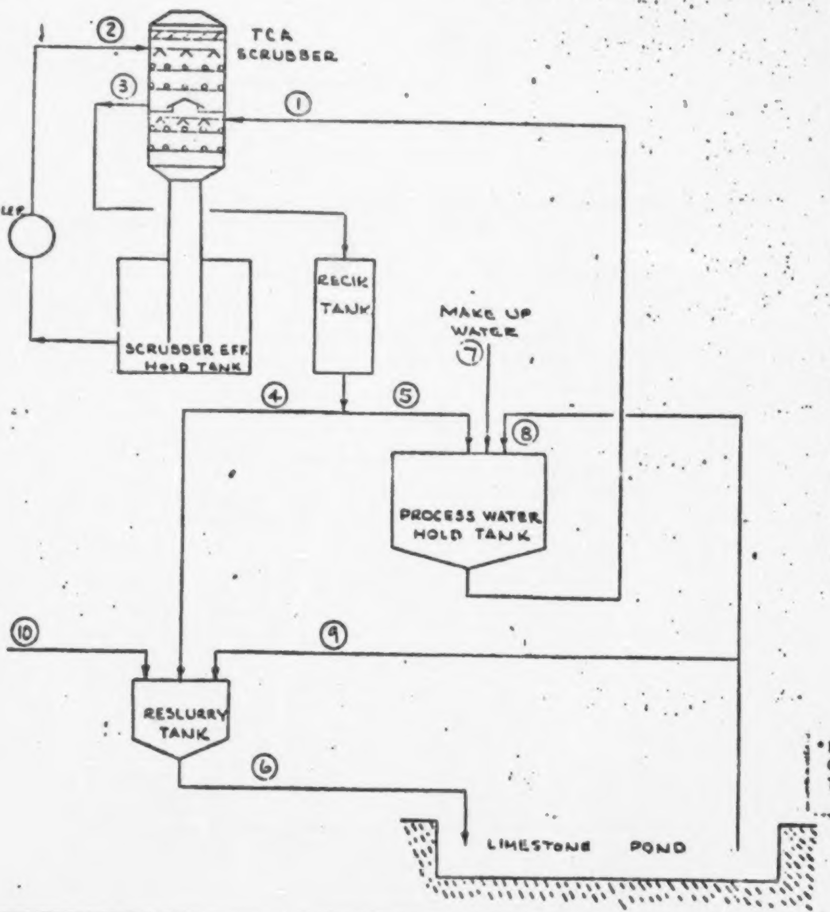
N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

TCA SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB NO.	DRAWING NO.	REV
6955	M-109-MS-6	0


②
③
TCA SCRUBBER
①
COOLER
SCRUBBER EFF. HOLD TANK
RECIR TANK
MAKE UP WATER ⑦
④
⑤
⑧
PROCESS WATER HOLD TANK
⑩
⑨
RESLURRY TANK
⑥
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	1400	2	1400	2	300	0			
2	[illegible]	2	[illegible]	2	275	0.4			
3	[illegible]	2	[illegible]	2	295	0.4			
4	850	2	[illegible]	2.5	295	0.4			
5	1000	2	[illegible]	2.5	0	0.4			
6	850	2	503	2.5	450	0.4			
7	20	0	13	0	7	0			
8	850	0	290	0	290	0			
9	250	0	200	0	152	0			
10	15	60	8	60	3	40			

FROM PLANT 100

OPERATING MODE
207

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	3/13	GEN REV
0		ISSUED FOR APPROVAL

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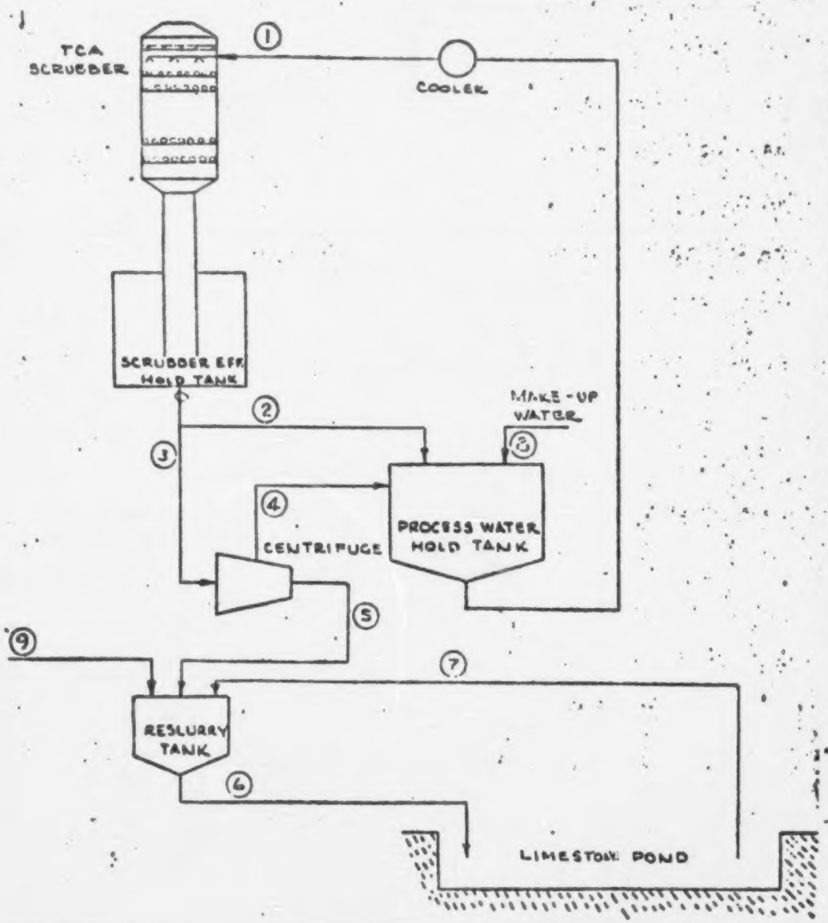
N. A. P. C. A.
ALKALI SCRUBBING TEST FACILITY

TCA SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB NO.	DRAWING NO.	REV.
6955	M-109-MS-7	0


TCA SCRUBBER
①
COOLER
SCRUBBER EFF HOLD TANK
②
③
MAKE-UP WATER
⑧
④
CENTRIFUGE
PROCESS WATER HOLD TANK
⑤
⑨
⑦
RESLURRY TANK
⑥
LIMESTONE POND

SLURRY FLOW DATA *

STREAM No	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	%S	GPM	%S	GPM	%S			
1	1400	15	1400	14	300	7			
2	1340	15	1340	14	250	7			
3	50	15	50	14	30	7			
4	45	.01	25	0	8	0			
5	25	28	25	28	4	28			
6	950	[illegible]	534	0.4	450	0.3			
7	950	0	500	0	442	0			
8	45	0	35	0	0	0			
9	10	60	9	60	4	60			

FROM PLANT 300

OPERATING MODE
208

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	5/13	GEN REV
0		ISSUED FOR APPROVAL

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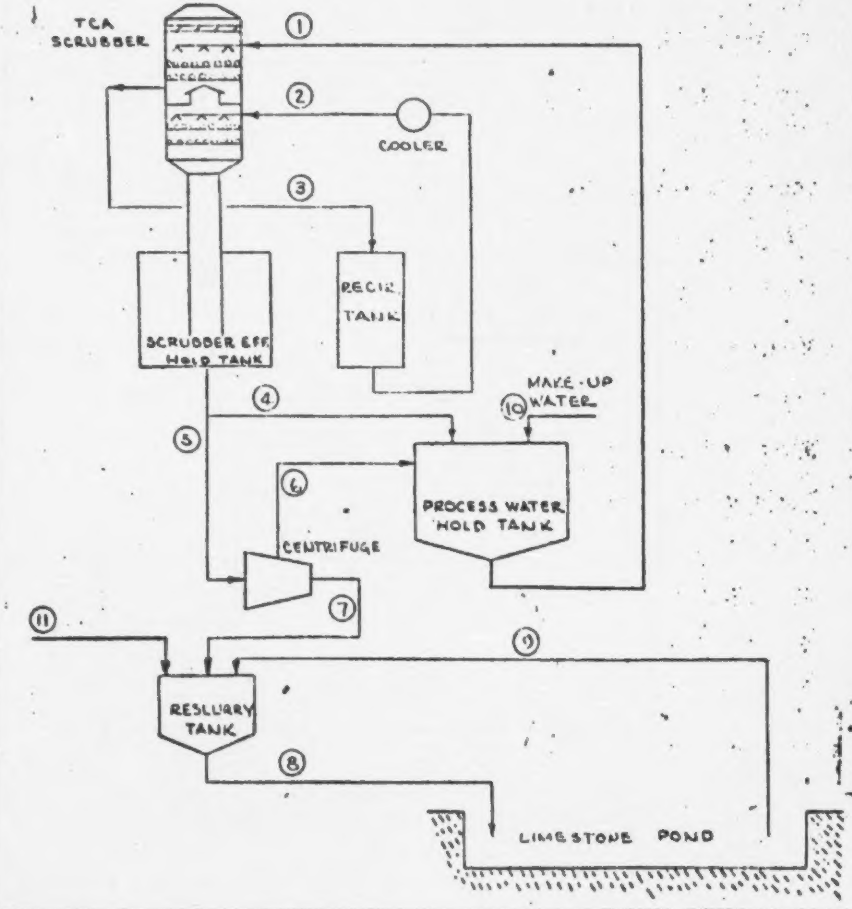
N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

TCA SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-109-MS-8	0


TCA SCRUBBER
①
②
COOLER
③
RECIR. TANK
SCRUBBER EFF. HOLD TANK
④
⑤
MAKE-UP WATER
⑩
⑥
PROCESS WATER HOLD TANK
CENTRIFUGE
⑦
⑪
⑨
RESLURRY TANK
⑧
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	1600	15	[illegible]	[illegible]	200	7			
2	[illegible]	15	1600	[illegible]	200	1			
3	[illegible]	[illegible]	[illegible]	14	50	7			
4	1340	15	34	14	250	7			
5	50	15	50	[illegible]	30	7			
6	40	0	25	0	8	0			
7	25	28	25	28	4	28			
8	850	0.5	533	0.4	450	0.3			
9	850	0	500	0	143	0			
10	45	0	35	0	8	0			
11	15	60	8	60	3	40			

FROM PLANT 100

OPERATING MODE
209

* NOT TO BE USED FOR DESIGN.
QUANTITIES SHOWN ARE FOR
TEST PROGRAM EVALUATION.

2							
1	5/23	GEN REV				WJ	
0		ISSUED FOR APPROVAL					

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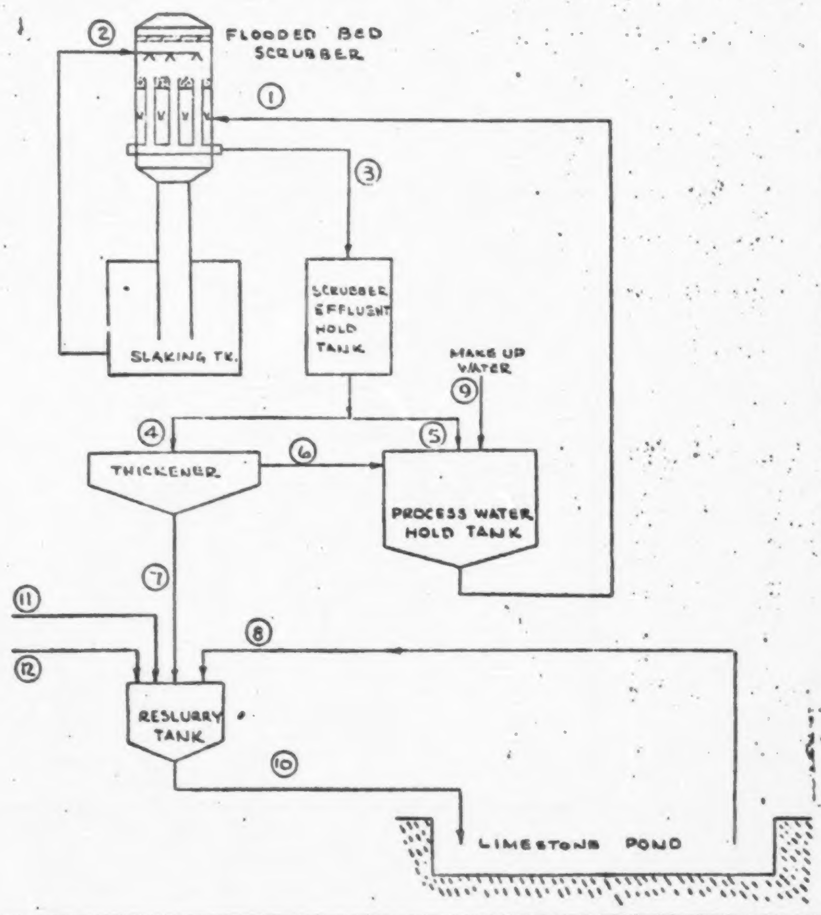
ALKALI SCRUBBING TEST FACILITY

TCA SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV.
6955	M-109-MS-9	


FLOODED BED SCRUBBER
①
②
③
SLAKING TK.
SCRUBBER EFFLUENT HOLD TANK
MAKE UP WATER
⑨
④
⑤
⑥
THICKENER
PROCESS WATER HOLD TANK
⑦
⑪
⑫
⑧
RESLURRY TANK
⑩
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	400	14	400	5	300	0	20	20	10
2	150	15	[illegible]	6	83	0.1	1	1	1
3	400	15	312	6	232	0.5			
4	400	15	100	6	15	0.5			
5	380	15	212	6	0	–			
6	365	01	83	0	0	0			
7	45	30	17	30	17	15			
8	850	0	500	0	412	0			
9	25	0	25	0	7	0			
10	850	02	542	01	450	[illegible]			
11	45	30	17	30	17	10			
12	8	60	8	60	4	60			

FROM PLANT 100
FROM PLANT 200

OPERATING MODE
301

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

1	5/2	GEN REV		
0		ISSUED FOR APPROVAL	IV	

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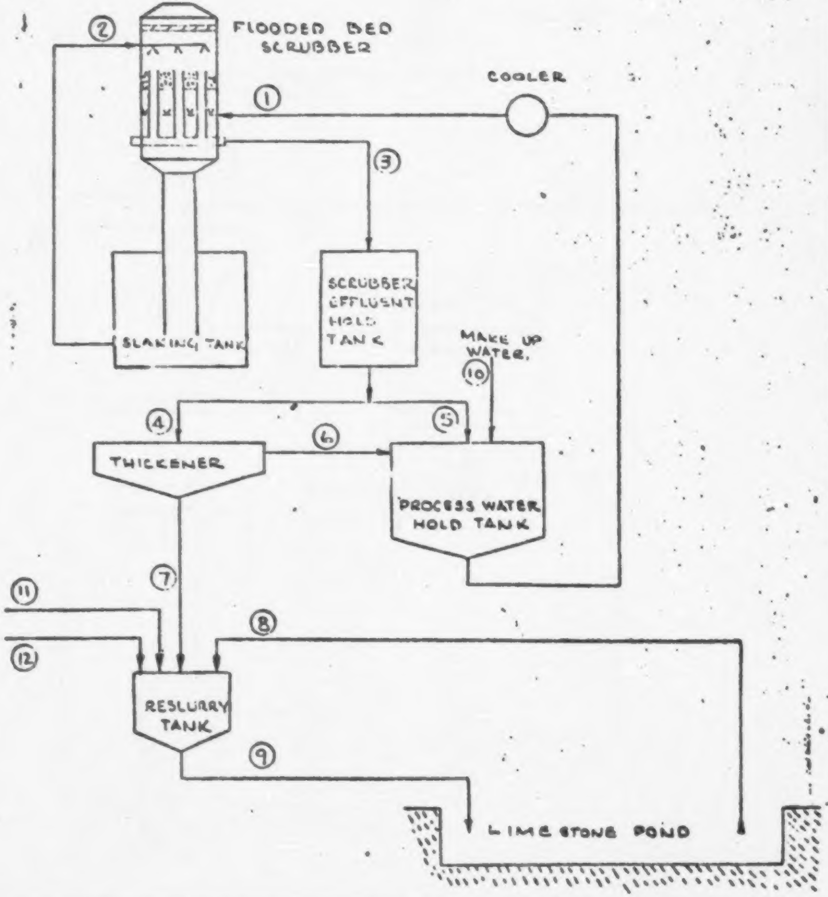
N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-110 - MS-1	0


FLOODED BED SCRUBBER
COOLER
SLAKING TANK
SCRUBBER EFFLUENT HOLD TANK
MAKE UP WATER
THICKENER
PROCESS WATER HOLD TANK
RESLURRY TANK
LIMESTONE POND
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	400	14	[illegible]	5	330	[illegible]	20	20	10	PLUS COOLER ΔP
2	150	15	100	6	80	0.5	1	1	1	
3	[illegible]	5	[illegible]	6	292	[illegible]				
4	400	[illegible]	100	6	15	[illegible]				
5	280	15	[illegible]	6	0	--				
6	365	0.1	83	0	0	0				
7	45	30	17	30	17	15				
8	850	0	500	0	427	[illegible]				
9	850	0.8	530	0.6	450	[illegible]				
10	25	0	25	0	7	0				
11	6	70	5	70	2	60				FROM PLANT 100
12	8	60	8	60	4	60				FROM PLANT 200

OPERATING MODE
302

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

△							
△	5/1	GEN REV					
△		ISSUED FOR APPROVAL					

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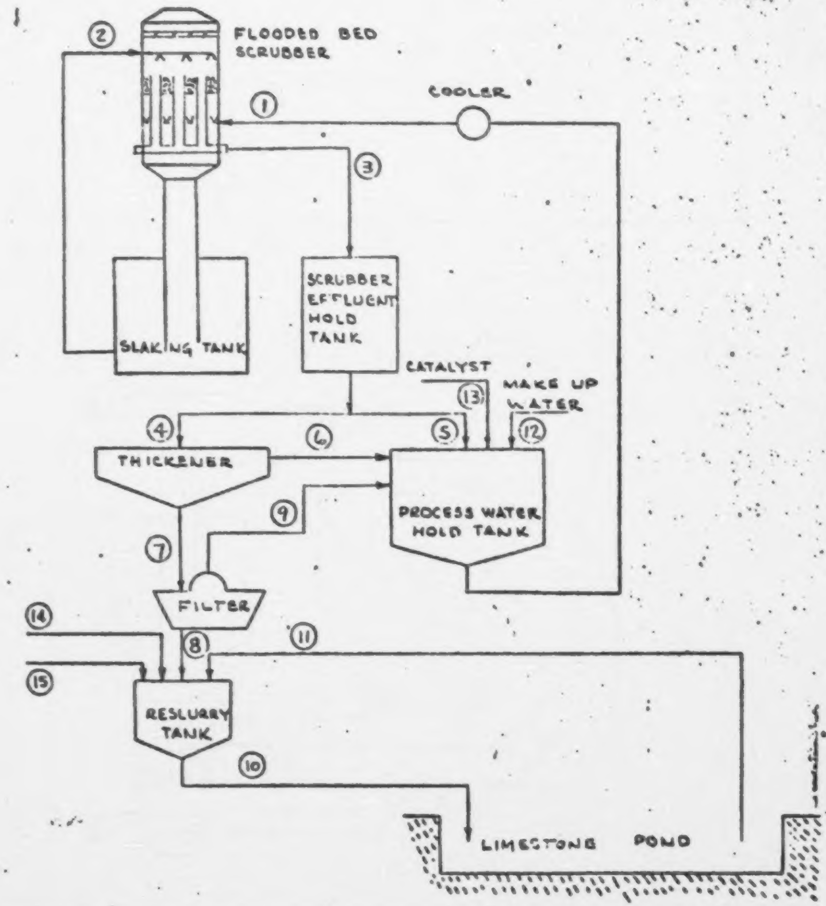
N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-110-MS-2	0


FLOODED BED SCRUBBER
②
①
COOLER
③
SLAKING TANK
SCRUBBER EFFLUENT HOLD TANK
CATALYST
⑬
MAKE UP WATER
⑫
④
⑥
⑤
THICKENER
⑨
PROCESS WATER HOLD TANK
⑦
FILTER
⑭
⑧
⑪
⑮
RESLURRY TANK
⑩
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	400	14	400	5	350	0	18	15	10	PLUS COOLER ΔP
2	150	15	100	8	100	0.5	1	1	1	
3	400	15	317	6	292	0.5				
4	400	15	100	6	15	0.5				
5	380	15	292	6	0	-				
6	305	.01	83	0	0	0				
7	45	30	17	30	17	15				
8	10	60	8	60	4	60				
9	42	0	9	0	8	0				
10	895	0.3	530	0.1	450	0.3				
11	850	0	500	0	427	0				
12	20	0	14	0	7	0				
13	3	0	2	0	1	0				(MILROY)
14	10	70	5	70	2	60				FROM PLANT 100
15	45	30	17	30	17	15				FROM PLANT 200

OPERATING MODE
303

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

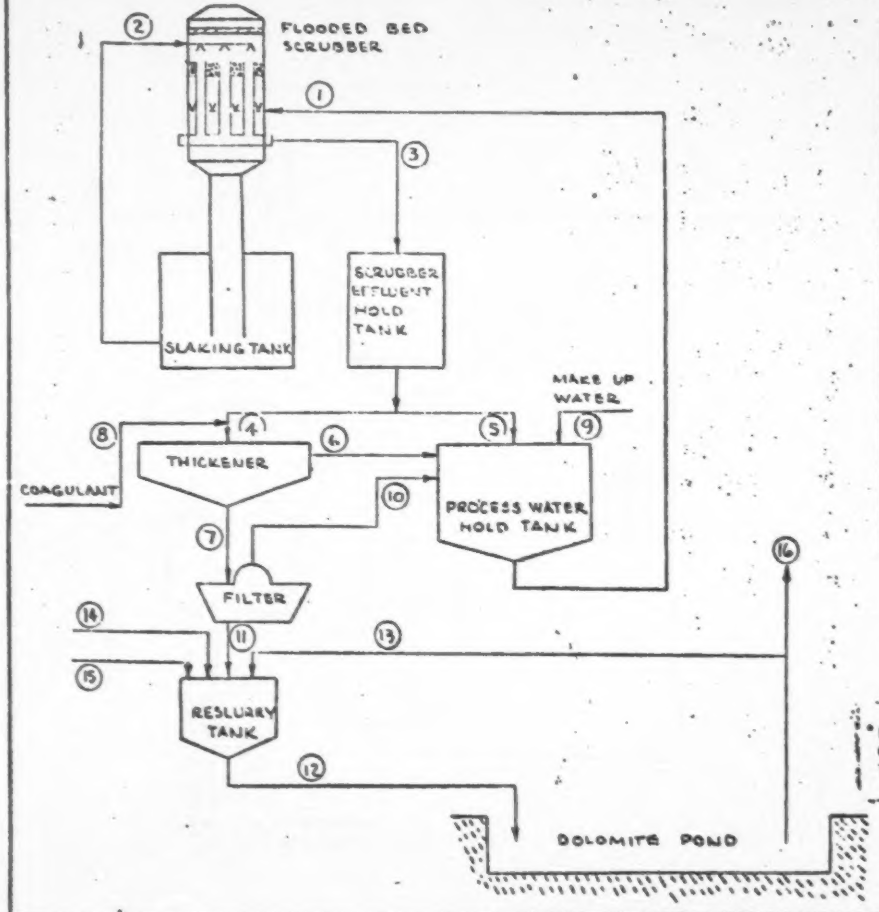
△			
1	9/72	GEN REV	
0		ISSUED FOR APPROVAL	

BECHTEL
SAN FRANCISCO

N. A. P. C. A.
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-110-MS-3	0


FLOODED BED SCRUBBER
②
①
③
SLAKING TANK
SCRUBBER EFFLUENT HOLD TANK
MAKE UP WATER
⑨
⑧
④
⑥
⑤
COAGULANT
THICKENER
PROCESS WATER HOLD TANK
⑩
⑦
FILTER
⑯
⑭
⑪
⑬
⑮
RESLURRY TANK
⑫
DOLOMITE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	400	14	400	5	360	0	18	15	10	
2	150	15	100	6	20	0.5	1	1	1	
3	400	15	392	6	[illegible]	0.5				
4	400	15	100	6	15	0.5				
5	350	15	292	6	0	–				
6	300	0.1	85	0	0	0				
7	45	30	17	30	17	15				
8	1	0	0.2	0	0	0				MILROY
9	20	0	16	0	7	0				
10	42	0	9	0	8	0				
11	15	60	8	60	4	60				
12	850	0.8	520	0.6	450	0.3				
13	850	0	122	0	50	0				
14	592	2.2	392	1.5	392	0.3				FROM PLANT 100
15	8	60	8	60	4	60				FROM PLANT 200
16	590	0	386	0	226	0				TO PLANT 100

OPERATING MODE
304

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

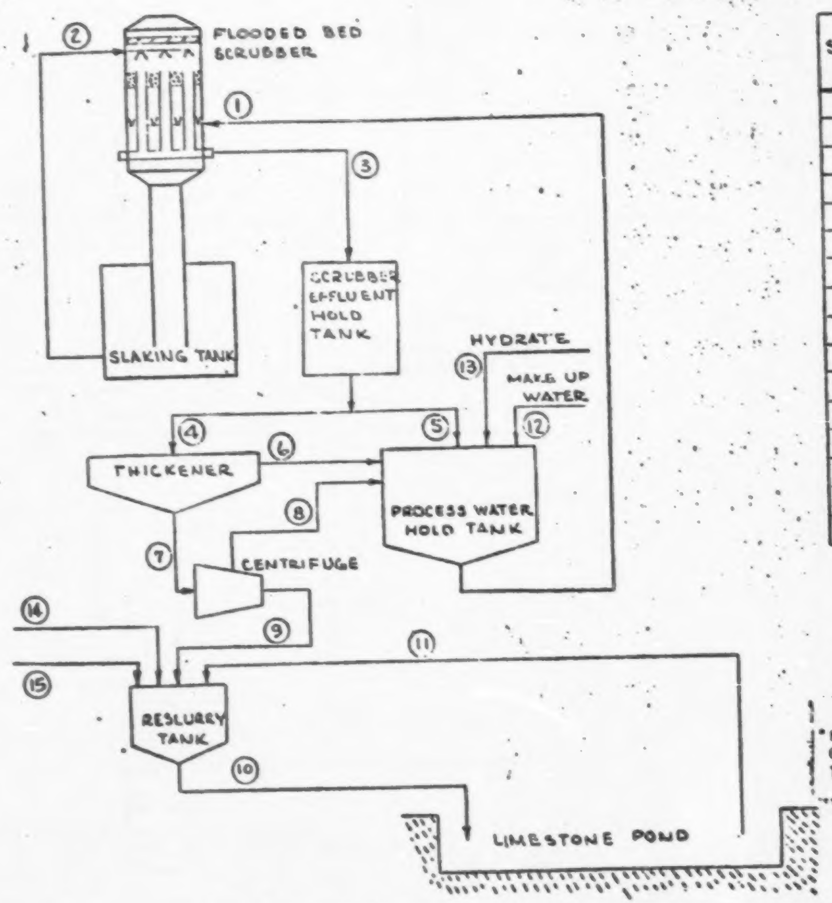
1	5/??	GEN REV	
0		ISSUED FOR APPROVAL	

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.
6955	M-110-MS-4


FLOODED BED SCRUBBER
②
①
③
SLAKING TANK
SCRUBBER EFFLUENT HOLD TANK
HYDRATE
⑬
MAKE UP WATER
⑫
④
⑤
⑥
THICKENER
⑧
PROCESS WATER HOLD TANK
⑦
CENTRIFUGE
⑭
⑨
⑪
⑮
RESLURRY TANK
⑩
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	400	15	400	5	300	0.3	12	15	10	
2	150	15	100	6	80	0.2	1	1	1	
3	400	15	392	6	292	0.2				
4	300	15	100	6	15	0.5				
5	392	15	292	6	0	-				
6	365	0.1	83	0	0	0				
7	45	30	17	30	17	15				
8	42	0.1	9	0	8	0				
9	10	60	8	60	4	60				
10	850	0.8	533	0.6	450	0.3				
11	850	0	500	0	425	0				
12	10	0	0	0	0	0				
13	30	25	16	5	10	5				MILROY
14	45	30	17	30	17	10				FROM PLANT 100
15	8	60	8	60	4	60				FROM PLANT 200

OPERATING MODE
305.

* NOT TO BE USED FOR DESIGN.
QUANTITIES SHOWN ARE FOR
TEST PROGRAM EVALUATION.

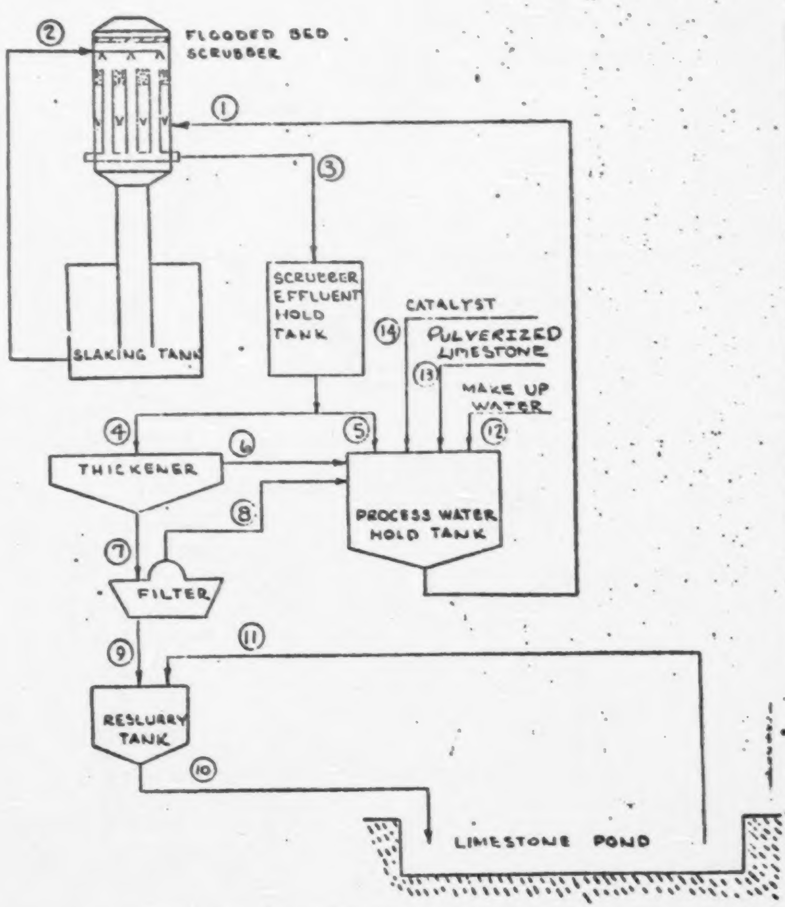
1	5/72	GEN REV	
0		ISSUED FOR APPROVAL	

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV
6955	M-110-MS-5	0


FLOODED BED SCRUBBER
②
①
③
SLAKING TANK
SCRUBBER EFFLUENT HOLD TANK
CATALYST
⑭
PULVERIZED LIMESTONE
⑬
MAKE UP WATER
⑫
④
⑤
⑥
THICKENER
⑧
PROCESS WATER HOLD TANK
⑦
FILTER
⑨
⑪
RESLURRY TANK
⑩
LIMESTONE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	%S	GPM	%S	GPM	%S			
1	400	15	400	5	300	0.3	18	15	10
2	150	15	100	6	80	0.2	1	1	1
3	400	15	312	6	292	0.7			
4	400	15	100	6	20	0.5			
5	385	15	292	6	0	–			
6	360	0.1	23	0	0	0			
7	45	30	17	30	17	15			
8	42	0	9	0	8	0			
9	10	60	8	60	4	60			
10	850	0.8	530	0.6	450	0.3			
11	850	0	522	0	446	0			
12	10	0	0	0	5	0			
13	30	25	14	5	10	5			
14	3	0	2	0	1	0			

OPERATING MODE
306

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

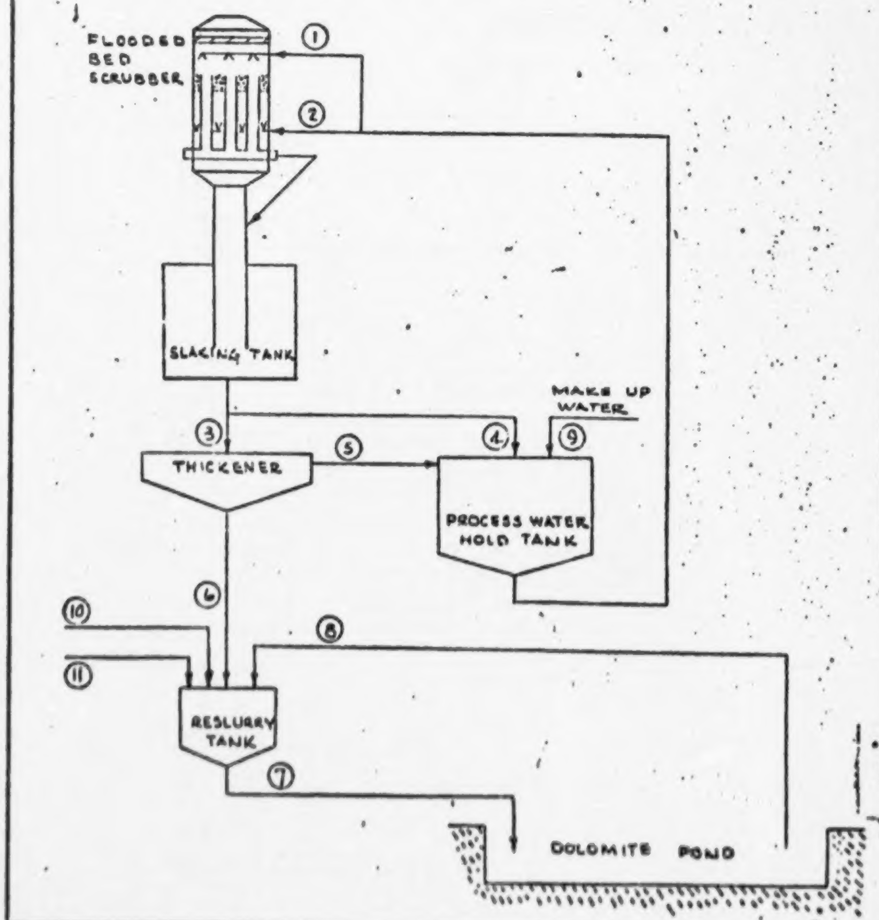
△			
△1	8/31	GEN. REV.	VMT
△0		ISSUED FOR APPROVAL	

BECHTEL
SAN FRANCISCO

N. A. P. C. A.
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB No.	DRAWING No.	REV.
6955	M-110 - M.S.-6	0


FLOODED BED SCRUBBER
①
②
SLAKING TANK
③
THICKENER
④
⑤
MAKE UP WATER
⑨
PROCESS WATER HOLD TANK
⑥
⑩
⑪
⑧
RESLURRY TANK
⑦
DOLOMITE POND

SLURRY FLOW DATA *

STREAM Nº	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	% S	GPM	% S	GPM	% S			
1	200	14	150	5	100	0	2	2	2
2	400	14	400	5	300	0	18	15	10
3	600	15	550	6	20	0.5			
4	350	15	200	6	0	–			
5	360	0.1	83	0	0	–			
6	45	30	17	30	17	15			
7	850	0.8	542	0.4	450	0.3			
8	850	0	500	0	412	0			
9	25	0	25	0	7	0			
10	45	30	17	30	17	10			FROM PLANT 100
11	8	60	8	60	4	60			FROM PLANT 200

OPERATING MODE
307

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

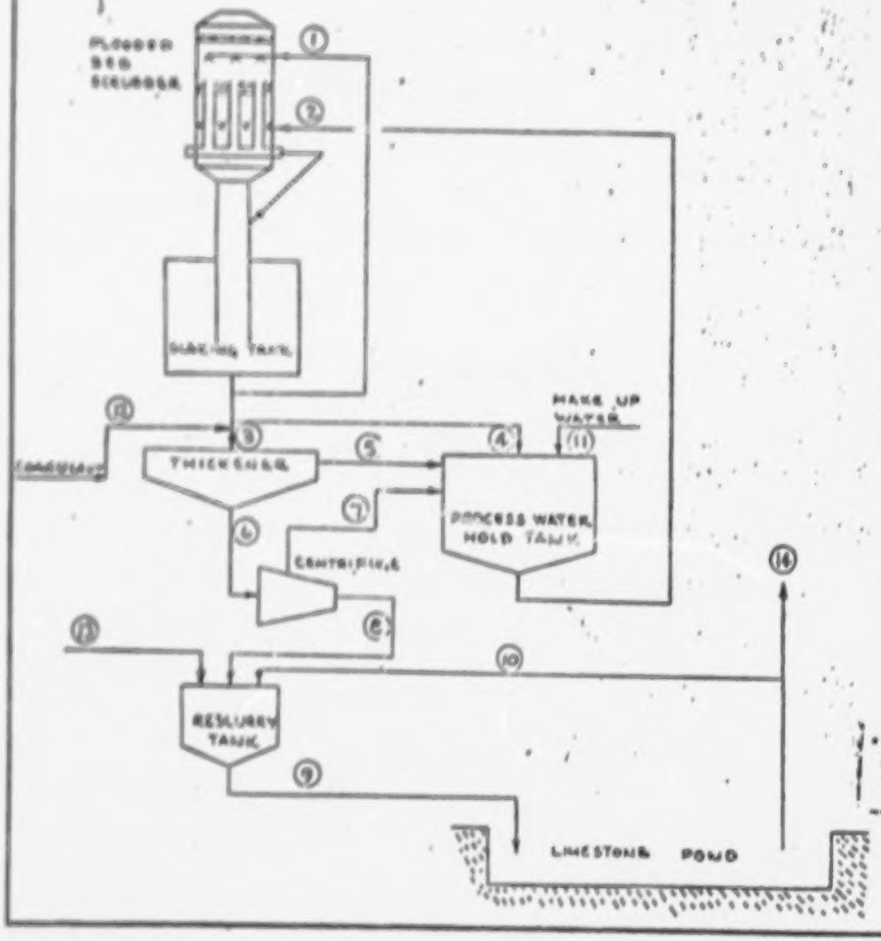
1 3/22 GEN REV
0 ISSUED FOR APPROVAL

BECHTEL
SAN FRANCISCO

N. A. P. C. A.
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

6955 M-110-MS-7 0


FLOODED BED SCRUBBER
①
②
SLAKING TANK
⑫
⑬
THICKENER
⑤
④
MAKE UP WATER
⑪
PROCESS WATER HOLD TANK
⑥
⑦
CENTRIFUGE
⑧
⑭
⑮
⑩
RESLURRY TANK
⑨
LIMESTONE POND

SLURRY FLOW DATA *

STREAM NO.	FLOW (GPM) & % SOLIDS						PRESSURE (PSIG)			
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.	
	GPM	% S	GPM	% S	GPM	% S				
1	200	14	150	5	100	0	2	2	2	
2	[illegible]	15	[illegible]	5	200	0.3	18	15	10	
3	660	15	[illegible]	6	30	0.5				
4	[illegible]	15	[illegible]	6	0	-				
5	365	01	83	11	0	-				
6	45	60	17	30	17	15				
7	42	01	9	0	8	0				
8	10	60	8	60	4	60				
9	836	9.8	530	9.6	450	0.3				
10	850	0	130	0	54	0				
11	20	0	16	0	7	0				
12	1	0	0.2	0	0	0				
13	592	2.2	392	1.5	392	0.3				FROM PLANT 100
14	590	0	386	0	386	0				TO PLANT 100

OPERATING MODE
30B

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

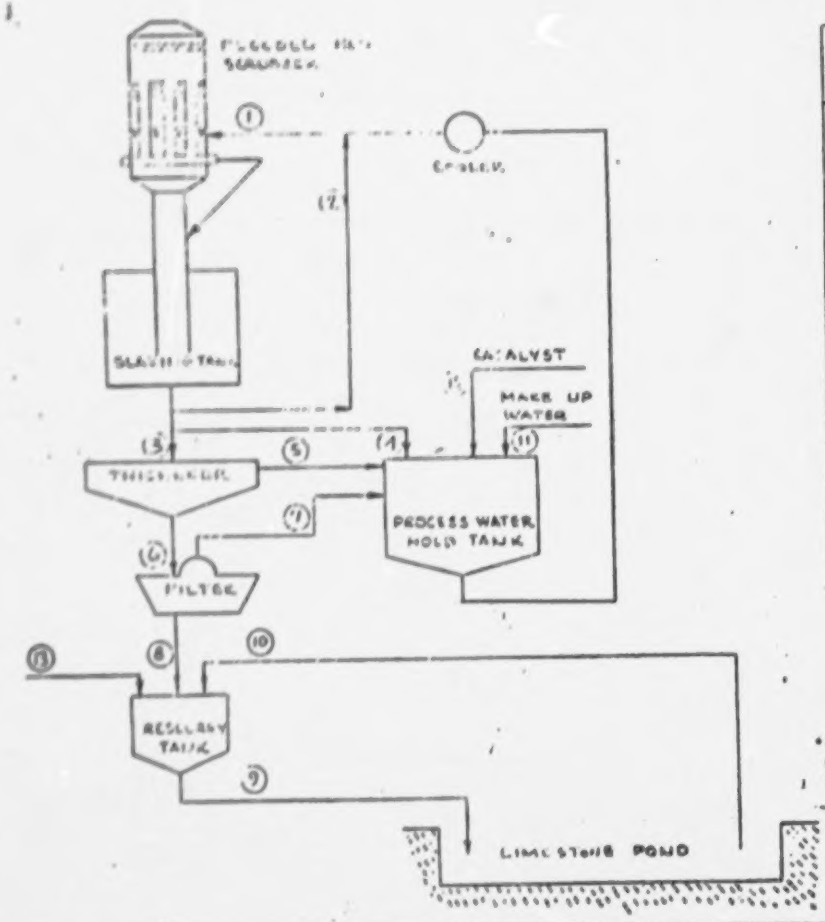
△		
△	1/11	GEN REV
△		ISSUED FOR APPROVAL

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

JOB NO.	DRAWING NO.	REV
6955	M-110-MS-8	0


FLOODED BED SCRUBBER
①
COOLER
(12)
SLURRY TANK
(3)
THICKENER
(5)
(4)
CATALYST
MAKE UP WATER
(11)
PROCESS WATER HOLD TANK
(7)
(6)
FILTER
(13)
(8)
(10)
RESLURRY TANK
(9)
LIMESTONE POND

SLURRY FLOW DATA *

STREAM NO	FLOW [GPM] & % SOLIDS						PRESSURE [PSIG]		
	MAX.		TYPICAL		MIN.		MAX.	NORM.	MIN.
	GPM	%S	GPM	%S	GPM	%S			
1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	23	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]	6	[illegible]	0.5			
3	[illegible]	[illegible]	[illegible]	6	[illegible]	0.5			
4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–			
5	[illegible]	[illegible]	[illegible]	6	[illegible]	0			
6	[illegible]	[illegible]	17	[illegible]	17	15			
7	42	0	8	0	8	0			
8	10	60	4	60	1	60			
9	[illegible]	[illegible]	517	26	450	[illegible]			
10	850	0	500	0	142	0			
11	32	0	32	0	7	0			
12	3	0	2	0	1	0			
13	10	60	8	60	4	60			

FROM PLANT 200

OPERATING MODE
309

* NOT TO BE USED FOR DESIGN. QUANTITIES SHOWN ARE FOR TEST PROGRAM EVALUATION.

ISSUED FOR APPROVAL

BECHTEL
SAN FRANCISCO

N. A. P. C. A
ALKALI SCRUBBING TEST FACILITY

FLOODED BED SCRUBBING SYSTEM
SLURRY FLOW SHEET

6955
M-110-1/5-9

APPENDIX D

DETAILED ASSESSMENT OF X-RAY ANALYTICAL METHODS

D.1 EVALUATION AND RECOMMENDATION OF X-RAY INSTRUMENTATION

As a result of the studies performed on this program, the Applied Research Laboratories (ARL) units were recommended for both laboratory and on-line use. The details of this review are presented below under the four following categories:

- Cost review of suitable X-ray instrumentation,
- Evaluation of technical capability of instrumentation,
- Manpower requirements for operation, and
- Preliminary specifications for X-ray instrumentation.

D.1.1 Cost Review of Suitable X-ray Instrumentation

Wavelength Dispersive Type Spectrometer

- Applied Research Laboratories (A.R.L.)

Model PCXQ 44000 (for on-line analysis of slurries)

Instrument Cost: a) Single stream without a computer, $70K
b) Fifteen streams without a computer, $100-110K
c) Fifteen streams with a computer, $150-160K

Computer Programming: $6K for 6 man weeks plus $0.2K per day as required

The PCXQ 44000 is the only instrument seen to date that could serve as an on-line analyzer for liquid slurries. The prices above are for units with a scanning spectrometer, six fixed spectrometers, and an external standard. The instrument operates with a helium x-ray path since elements lighter than manganese will be included in the analytical program.

Model VXQ 25000 with 46000 Console (LAB Unit)

Instrument Cost: a) ~$60K with computer capability
b) ~$90K includes computer (HP 2114C)

The VXQ 25000 laboratory unit priced above would include a scanning spectrometer, six fixed spectrometers, and an external standard. This instrument can operate in the manual or automatic mode in helium or vacuum.

Model VXQ 25000 with 245000 Console (LAB Unit)

Instrument Cost: a) Single scanning spectrometer, $41K
b) Up to 4 fixed spectrometers, add $1.5K each
c) Six fixed spectrometers installed, add $2.2K each

The VXQ 25000 with the 245000 console includes a scanning spectrometer, a variable number of fixed spectrometers, and an external standard. It is a unit that can be operated manually or automatically. Readout is in direct % concentrations on a single-sheet hard copy.

Purchase of any of the A.R.L. instruments entitles one person to go to a tuition-free X-ray school for one week at A.R.L. Also, training is provided during the plant checkout and installation of the equipment.

- General Electric (G.E.)

Model XRD-710 (Automatic Lab Unit)

Instrument Cost: ~$90K including computer

The XRD-710 instrument is a fully automated, solid state unit capable of sequentially analyzing 10 specimens for 49 elements from F upwards. Operation is in vacuum or air.

Model XRD 700VS (Manual Lab Unit)

Instrument Cost: a) ~$32K with a four specimen sample holder
b) ~$41K with a ten specimen sample holder

The XRD 700VS is strictly a manual unit operable in air or vacuum.

Energy Dispersive Type Spectrometer

- Kevex Corporation

  Model - Vacuum System (Lab Unit)

  Instrument Cost: a) ~\$22K without a computer
  b) ~\$35K with a computer

  The Kevex instrument has limited detectability and probably the least versatile instrument of those evaluated.

D.1.2 Evaluation of Technical Capability of Instrumentation - Instrumentation provided by the ARL, GE and Kevex vendors has been evaluated for technical capability to satisfy process monitoring requirements of the wet limestone injection sulfur dioxide abatement process. Key points in this evaluation which distinguish the instrumentation from each other are presented below.

General Electric Instrumentation - The evaluation of the G.E. instrumentation was accomplished through discussions with applications personnel and assessment of the technical ability of the instrument for the job. TRW laboratory specimens were not used because of a long lead time necessary to acquire experimental data. Four G.E. wavelength dispersive X-ray spectrometer systems were evaluated, 1) XEG - X-ray Emission Gage I for computerized process control, 2) 700VS manual laboratory unit, 3) XRD-410 vacuum tube automated laboratory unit, and 4) XRD-710 solid state automated laboratory unit. Distinguishing features of these instruments are:

- The XEG unit was designed for dry powders only. Two slurry units were sold by G.E. and they are a constant problem.
- A slurry presenter is not feasible with any of the G.E. units.
- G.E. has no automated equipment to convert slurries to briquettes. In fact, they stated that an on-line slurry dryer would not result in an efficient operation.
- All G.E. units discussed utilize the more inefficient flat diffracting crystals as opposed to the curved diffracting crystals used in Applied Research Laboratory Equipment.

In summary, no G.E. unit can be utilized for on-line process control of wet scrubbing process slurries. Their instrumentation should, however, be considered for use in a laboratory environment.

Kevex Instrumentation - These comments are the results of discussions with Mr. Richard S. Frankel, President, and Dr. Rolf Woldseth, Applications Lab Director on 7, 19, 20 and 24 May 1971 and on 9 June 1971. The data presented (see Table VIII - Section 2.4) were obtained by Dr. Woldseth on the same TRW prepared specimens which were analyzed previously by Applied Research Laboratories. The following points were developed from the contacts made with Kevex Corporation:

- There is a basic problem with regard to the detection of low levels of S in a matrix containing a high level of Ca with energy dispersive X-ray spectrometer systems such as those sold by Kevex. That basic problem is that the CaKβ escape peak of 2.27 KeV interferes directly with the SKα_1 peak at 2.27 Kev. This escape peak phenomenon occurs in the Si(Li) X-ray detector when 4.01 KeV Cakβ_1 quanta ionize the Si and cause 1.74 KeV SiKα_1 X-rays to escape from the detector and leave 2.27 KeV quanta to be counted. The effect of the CaKβ escape peak was demonstrated at Kevex with TRW specimen 009, limestone/Zurn FA, containing 0.045 ± 0.015% w/w S by wet chemical analysis at TRW. The sulfur determination data on specimen 009 were as follows for a 100 second count:

Gross count	655
Background count	510
Net count	145
Ca Escape Peak count	130

  The 145 net counts and 130 calcium escape peak counts are well within the counting statistical error of approximately 30 counts. The conclusion was that in this case the Kevex unit used was not capable of detecting sulfur down to the 0.03 - 0.06% w/w level. The vacuum path Kevex unit could probably detect S in a limestone matrix to the 0.3 - 0.5 ± 0.1% w/w level, i.e., a factor of 10 to 20 times worse than the ARL 72000 Quantometer. The sensitivity of the Kevex instrument could be improved by a factor of > 5 by counting for a longer time than 100 seconds, using a 50μCi source rather than the 25μCi Fe^{55} used, and using an 80 mm detector instead of the 30 mm detector used.

- As in the case of wavelength dispersive X-ray spectrometers (G.E. and A.R.L. instruments) the output signal is influenced by specimen particle size. Particles sized below $\sim$250 microns can usually be analyzed accurately by X-ray instrumentation.

- Kevex Corporation has no slurry presenter equipment.

- Kevex Corporation has no computer software available. All computer interfacing must be with their supplier, Nuclear Data, Inc.

- The A.R.L. unit detected Mg known to be present in more than half of the 14 TRW specimens submitted; the Kevex unit detected no Mg.

In summary, no Kevex unit, like G.E., can be used for on-line control of wet scrubbing process slurries. In addition, their instrumentation is somewhat limited even in a laboratory environment and does not compete well with either the A.R.L. or G.E. units considered.

Applied Research Laboratory X-ray Instrumentation - The evaluation of the A.R.L. X-ray instrumentation was based on results of TRW prepared specimens. The A.R.L. wavelength dispersive X-ray spectrometer instrumentation has several advantages over G.E. and Kevex equipment. These advantages are:

- Curved diffracting crystals are used which are more efficient than flat crystals used by G.E., i.e., their use results in higher count rates, thereby allowing shorter count times than with flat crystals.

- Up to nine elements can be determined simultaneously since A.R.L. has capability for nine fixed spectrometers.

- An external standard in A.R.L. instruments automatically corrects for changes in X-ray tube voltage.

- A.R.L. has the only available and proven slurry presenter apparatus.

- A.R.L. has a patented slurry density gauge as an integral part of their on-line equipment.

X-ray Instrument Availability

A.R.L.	90 - 120 days without computer 120 - 150 days with computer
G.E.	90 - 120 days
Kevex	60 days

D.1.3 Manpower Requirements for Operation - The manpower requirements listed here are approximations based on experience and discussions with the three vendors. Initially, perhaps for the first three months of operation, any X-ray instrument will require one full time engineer or scientist and one technician per shift. After the initial period, engineer time should decrease to approximately 50% over perhaps the next nine months of operation; technician time should remain at one man per shift. In fact, 50% of an engineer's time for one shift per day should be adequate after a year's operation; the other shifts could be run with one technician.

With computerized data acquisition and reduction equipment, it is estimated that the following maximum number of analyses and elements per analysis could be obtained for the four X-ray equipment operational modes:

X-Ray Unit	Estimated Maximum Number of Analyses per 8-hour Shift	Number of Elements Per Analysis	Total Elemental Analyses
A.R.L. (on line)	240[a]	8	∿1800
A.R.L. (lab)	160[a]	7	∿1000
G.E. (lab)	160[a]	1	∿160
Kevex (lab)	45[b]	∿50 (16)	∿640

[a] Two-minute residence period in spectrometer

[b] Ten-minute residence period in spectrometer

Unfortunately, of the 50 elements possible with the Kevex unit, only about 16 are of primary interest to the limestone injection wet scrubbing sulfur dioxide abatement process.

Using the above estimates, the number of elemental analyses per 8-hour shift, taking equipment maintenance requirements (5% down time) into account, are estimated as follows:

A.R.L. (on-line)	~1800 elemental analyses
A.R.L. (lab)	~1000 elemental analyses
G.E. (lab)	~160 elemental analyses
Kevex (lab)	~640 elemental analyses

It is emphasized that these numbers are maxima and were calculated under the assumption that the operation was quite routine and well-trained personnel had been working the problem for about one year.

In addition, the calculations assume that there is a plentiful supply of separated or non-separated slurry for analysis to ensure that the maximum number of analyses per 8-hour shift is maintained. This assumption can lead to high labor costs for acquisition of samples, separation, and transfer to the laboratory while maintaining documented inventory and clean-up prior to the next set of samples.

For the purpose of providing a cost of operation estimation, it is assumed that five sampling points on each of the three scrubber units are to be sampled every 30 minutes (total 30 samples/hour). Similar calculations can be made for other combinations resulting in 30 samples/hour rate (e.g., 6 sampling points on one scrubber every 12 minutes). A summary of the mechanical operations to be performed by technician labor are as follows:

Operation	Estimated Time Required, Minutes
1. Install grab sampler unit on scrubber	3
2. Take sample*	2
3. Remove grab sample*	2
4. Perform separation	2
5. Take sample to laboratory	6
6. Log sample with identification number	1
7. Load sample into X-ray carousel sample compartment	2
8. Remove sample	2
9. Clean grab sampler	2
10. Take sampler to scrubber	6
	28

*When Demco/filter combination is used, these numbers are reduced but not eliminated because it is necessary to purge the system with the stream.

Although the total time is 28 minutes/analysis, several operations (such as Steps 5, 9, and 10) can be combined with other samples and, hence, it is estimated that 8 to 9 technicians can provide an adequate number of samples providing the operations can be programmed so that the technicians do not run into each other. With the 10-minute residence time requirement of the Kevex, fewer samples are required (6 per hour) and, hence, only two technicians are required for sampling. A summary of estimated costs for operation and acquisition of X-ray instrumentation is shown in Table D-I. Costs required for computer operation are not included in these numbers, however, it is readily seen that the costs associated with the two A.R.L. units provide more cost effective operation.

D.1.4 Preliminary Specification for X-ray Instrumentation - The instrument sensitivity standardization computer interfacing and minimum required computer software for X-ray instrumentation suitable for both on-line and laboratory use are comparable. Specific requirements for these two operation modes have unique requirements in number of spectrometers and analytical speed. The general and specific specification requirements are presented below.

General Specification

Sensitivity and Precision

The instrument will be able to detect all elements above atomic number 11 in concentrations down to 0.1 % w/w. Water slurries with 1, 5 and 10% w/w solids (limestone and dolomite matrices) will be analyzed to demonstrate specific sensitivity to Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, and Fe in both the liquid and solid phases. The precision must be at least 2% of the measured value.

Computer Interfacing

The instrument will interface with a computer supplied as part of the system. Output will be typewritten hard copy.

Minimum Required Software

Computer software is required to 1) control the sequence and functioning of all devices in the system, 2) convert elemental

TABLE D-I

SUMMARY OF ESTIMATED COSTS ASSOCIATED WITH OPERATIONS AND ACQUISITION X-RAY INSTRUMENTATIONS

		Operational Cost/8-Hour Shift									
		X-ray Unit Cost			Sampling Cost						
X-ray Unit	Capital Cost $K	MPS Hrs.	TS Hrs.	$[a]	TS Hrs.	$[a]	Total Cost $	Total Analyses	Total Elements	Cost/ Analysis $	Cost/ Element $
A.R.L. (on-line)	160	8	8	240	8	80	320	240	1800	1.33	0.18
A.R.L. (lab)	90	8	8	240	72	720	960	160	1000	6.00	0.96
G.E. (lab)	90	8	8	240	72	720	960	160	160	6.00	6.00
Kevex (lab)	35	8	8	240	16	160	400	45	640	8.88	0.62

[a] Calculated assuming a burdened labor cost for professional employees (MPS) of $20/hour and technicians (TS) of $10/hour.

count or voltage ratio output to percent concentration, 3) determine up to six interelement correction constants, 4) apply interelement correction constants to compensate for interelement effects, and 5) determine working curves from standard samples with graphic print out.

Specific Specifications

On-Line System Description

The on-line X-ray instrumentation will provide elemental composition analyses of flowing slurries in a minimum of three streams. Elemental readout will be typewritten in percent concentration. Elements with atomic numbers greater than 11 will be able to be analyzed automatically. There will also be provisions to analyze dry and wet batch specimens.

Analytical Speed

Approximately 1800 elemental analyses with elemental percent concentration output on hard copy must be feasible during an 8-hour shift. (Manpower: 1 laboratory technician).

Number of Spectrometers

There will be one scanning spectrometer and six fixed spectrometers for Mg, S, Cl, K, Ca, and Fe.

Instrument Standardization

Means will be provided to correct for minor variations in the X-ray tube power output during analysis.

Slurry Flowrate

The slurry presenter system will maintain a constant flow through the analyzer cell of 5 liters/minute.

Slurry Density

A means will be provided to determine the percent solids in the flowing slurry.

Laboratory System Description

The laboratory X-ray instrumentation will provide elemental composition batch analyses of slurries and dry solids. Elemental readout will be on hard copy in percent concentration. Elements with atomic numbers greater than 11 will be able to be analyzed using a vacuum or helium X-ray path.

Analytical Speed

Approximately 1000 elemental analyses with elemental percent concentration output on hard copy must be feasible during an 8-hour shift. (Manpower: 1 laboratory technician).

Number of Spectrometers

There will be one scanning spectrometer.

Instrument Standardization

Means will be provided to standardize the instrument.

Summary - In conclusion, it must be reiterated that the A.R.L. on-line X-ray unit is the most cost effective and pays for its capital cost with respect to the second most cost effective unit (A.R.L. lab) after only 105 8-hour shifts (using the assumptions employed to generate Table VI). Consequently, this on-line A.R.L. X-ray unit is tentatively recommended for process characterization of the limestone wet scrubbing sulfur dioxide abatement process. Should it be decided that a laboratory unit be employed, it is recommended A.R.L. lab instrument be purchased.

D.2 X-RAY FLUORESCENCE CHARACTERIZATION OF ACTUAL AND SIMULATED SOLIDS AND LIQUIDS FROM POWER PLANTS

D.2.1 TVA Samples

The five liquid samples and six solid samples submitted by J. Barkley of TVA were analyzed quantitatively by x-ray fluorescence techniques employing TRW's G.E. Model XRD-5 laboratory x-ray spectrometer. It is understood that, 1) these samples were intended to simulate a wide range of sample compositions, both liquid and solid phases, that could be encountered under varying wet scrubber operating conditions and, 2) these analytical results would provide additional information to aid TVA in their efforts to evaluate candidate analysis techniques.

In order to eliminate the effect of disparate particle size between standards and the unknown material, both were pulverized further and passed through a 325 mesh sieve (>44 micron particle size). In previous studies it was found that fluorescence intensity increased asymptotically with decreasing particle size reaching a plateau in the range of 70-100 microns.

The unknown samples were blended in a Wig-L-Bug and pelletized under 25,000 psi into a 1.5 in. diameter disc in a polyvinyl acetate ($\sim$0.1% wt) binder. Calibration curves for Ca, K, Cl, S, Fe were prepared using reagent grade anhydrous $CaCO_3$, K_2CO_3, NaCl, $CaSO_4$ and iron powder in a simulated fly ash/SO_2 reacted limestone background composed of SiO_2 and Al_2O_3.

The solution standards were prepared from reagent grade $Ca(NO_3)_2 \cdot 4H_2O$, Na_2SO_4, KCl and NaCl. The special liquid cell with Mylar window was employed for liquid analysis. Instrument operating settings were the same for both liquids and solids, as follows:

Tube - Cr operated at 50 KVP, 30 Ma
Crystal - PET
Purge gas - He
Detector - flow proportional
Counting time - 10 or 100 sec. depending upon elemental concentrations

The taken and measured concentrations for Ca, K, Cl, S and Fe together with a comparison of TVA's reported pH values to TRW's measured pH values are listed in Table D.II. The taken element values for the solid samples were derived from the compound blends defined by TVA which are given in Table D.III. For the liquid samples, the agreement between taken and found for Ca and K is excellent while the chloride values are somewhat more divergent. XRF sensitivity to sulfur, as discussed in several previous reports, is below the concentration made up. It is quite apparent that solutions 2, 3 and 4 have changed on standing as evidenced by the marked differences in pH.

The utility of XRF for this specific application is exemplified by the findings of the solids analysis. Upon superficial examination, the agrerment for Ca and S values appears rather poor. Closer study of the calcium data reveals that the measured concentrations are consistently higher than the reported taken values. The differences between the individual pairs are, however, proportional to the ash content, i.e., (text continued on Page 183)

TABLE D.II

QUANTITATIVE X-RAY ANALYSIS OF LIQUID AND SOLID SCRUBBER SAMPLES FROM TVA

	TVA Reported Values					TRW Measured Concentrations				
	Molality($X10^3$)									
Liquid Samples	Ca	K	Cl	S	(pH)	Ca	K	Cl	S	(pH)
#1	5.76	2.26	8.07	5.83	(6.8)	5.6	2.1	10.4	<9.4	(6.7)
#2	3.78	2.44	11.6	5.48	(5)	4.0	2.4	15	<9.4	(3.2)
#3	5.84	2.71	15.1	7.86	(6)	5.5	2.5	14	<9.4	(3.3)
#4	3.93	2.53	12.24	5.12	(7)	4.0	2.7	14	<9.4	(5.7)
#5	3.39	1.63	11.14	4.84	(7)	3.4	1.6	9.6	<9.4	(6.9)

% By Weight

Solid Samples	Ca[a]	K	Cl	S[a]	Fe	(Ash)	Ca	K	Cl	S	Fe
#1	10.5	-	-	4.9	-	(64.95)	16.1	1.2	<.002	6.5	16.5
#2	29.5	-	-	10.0	-	(3.99)	30.1	<.2	<.002	12.7	.9
#3	24.0	-	-	8.6	-	(30.1)	26.1	0.7	<.002	10.9	7.1
Hold Tank Outlet	-	-	-	-	-		7.2	1.3	.008	4.7	12.4
Clarifier Bottom ppt.	-	-	-	-	-		15.0	0.9	<.002	8.6	13.2
Clarifier Inlet	-	-	-	-	-		30.0	<.2	.009	12.2	1.7

[a] See Table D.III for prepared composition by compound

TABLE D.III

TVA SOLID SAMPLE COMPOSITION BY COMPOUND

	Sample No. 1			Sample No. 2			Sample No. 3		
	Wt %	Ca	S	Wt %	Ca	S	Wt %	Ca	S
$CaSO_4 \cdot 2H_2O$	25.00	5.81	4.65	51.04	11.87	9.50	40.07	9.32	7.46
$CaSO_3 \cdot 1/2H_2O$	0.91	0.28	0.22	2.05	0.64	0.51	4.84	1.50	1.20
$CaCO_3$	1.59	0.64	-	36.27	14.50	-	12.00	4.80	-
Ash	64.95	-	-	3.99	-	-	30.08	-	-
CaO	5.27	3.76	-	3.78	2.70	-	11.74	8.39	-
$MgCO_3$	1.00	-	-	2.98	-	-	0.89	-	-
Total:	98.72	10.49	4.87	100.11	29.71	10.01	99.62	24.01	8.66

Sample	Taken	Calcium Found	Absolute Δ	Ash	Relative Error Corrected for Ash Ca Contribution
No. 2	29.5	30.1	0.6	3.99	1.0%
No. 3	24.0	26.1	2.1	30.1	1.5%
No. 1	10.5	16.1	5.6	64.95	0.6%

Indeed, calculation of the least squares straight line equation using:

Y = fraction of total Ca
X = fraction of ash

gives; intercept, a = 0.317847 $\sigma = 0.000263$
slope, b = -0.232775 $\sigma = 0.016217$

and

X	Y
0.0399	0.30856
0.301	0.24778
0.650	0.16666
1.000	0.08507

Even considering the inhomogeneity of the added fly ash, the precision is good yielding a calculated calcium content in the fly ash of 8.51%.

The sulfur disparities were more of an enigma, as they did not lend themselves to easy explanation. Again, the concentrations found were consistently higher than the taken levels but the differences were inversely proportional to the ash content. A masking or antagonistic interference was considered but discarded because of the lack of consistency or correlation with the constituent levels. Assuming the analyses to be correct, it was next postulated that, rather than an experimental weighing error made in preparing the samples, another sulfate salt was used. Recalculation of the sulfur taken on the basis of anhydrous calcium sulfate gave the following correlation.

	$CaSO_4$(%S) + $CaSO_3\cdot 1/2\ H_2O$(%S) = New Taken %S	% Found
No. 1	(5.86)+(0.22) = 6.08	6.5
No. 2	(11.97)+(0.51) = 12.48	12.7
No. 3	(9.40)+(1.20) = 10.60	10.6

These data strongly suggest that the anhydrous sulfate salt was used as opposed to the reported dihydrate. Most importantly, the XRF tool is sufficiently accurate to allow elucidation of such anomalies.

D.3 DUKE POWER COMPANY SAMPLES

Several filter and impinger samples were submitted through the Project Officer for characterization by XRF and other techniques. The sample designations, elements determined by XRF and concentration values measured are listed below. Whereas the emphasis in this program has been directed toward Ca, Mg and S, note the utility for other pollutant species that are of concern in terms of human health, crop and material damage notably silicon phosphorous and chloride.

	Element, % by Weight			
Sample	Cl	S	Si	P
"B" Filter Paper	<0.1	3.7	16.5	0.65
Run 1-B				
Probe-Cyclone Acetone	2.2	1.8	12.7	0.42
Filter #12376	<0.1	1.0	13.5	0.35
Number 44	0.64	2.3	14.7	0.54

APPENDIX E

TENTATIVE METHOD FOR ANALYSIS FOR SULFITE AND BISULFITE ION BY FURFURAL BLEACHING

(A Laboratory Instrumental Method)

SCOPE

This method is applicable for the analysis of sulfite and bisulfite ion in aqueous media. While the method was developed especially for sulfur dioxide scrubbing processes, it has general applicability within the given ranges.

SUMMARY

An amount of sulfite and bisulfite ion adjusted to be in the concentration range of 1-5 *mM* is added to a measure excess of furfural. A none UV-absorbing complex is formed and from a measurement of the decrease in absorbance of the free furfural species at 276 *nM* and pH 4, the bisulfite concentration can be calculated utilizing standard spectrophotometric calibration techniques.

REAGENTS

1) Furfural Solution, Aqueous, approximately 2.5×10^{-4} M

Dissolve 24 mg ± 2 mg in deionized water which has been boiled to remove oxygen and cooled. Dilute to one liter in a volumetric flask. This reagent should be made fresh daily and used for preparation of a standard curve using standard known bisulfite solutions.

2) NaH_2PO_4 Buffer Solution

Dissolve 120.0 grams of reagent grade NaH_2PO_4 in 1 liter of boiled, cooled, deionized water. Adjust pH to 4.0 by dropwise additions of concentrated H_3PO_4. This solution is stable and does not have to be freshly made.

3. Aqueous Sulfamic Acid

Dissolve 0.486 g of reagent grade NH_2SO_3H in 200 ml of boiled, cooled, deionized water.

NOTE: Minimize air exposure of all reagents.

REQUIRED EQUIPMENT

1. Beckman DK-2A ultraviolet-visible spectrophotometer or equivalent.
2. Matched silica sample cells with an optical path length of 10 mm.

PREPARATION OF STANDARD CALIBRATION CURVE

The separation of the standard bisulfite solutions and absorbance curve should be carried out each day that samples are analyzed. Weigh a quantity of reagent grade sodium bisulfite to be determined by the formula:

$$\text{Grams } NaHSO_3 = \frac{16.0}{\%SO_2}$$

where $\%SO_2 = \%SO_2$ in the $NaHSO_3$ (SO_2 content is the normally reported assay value for $NaHSO_3$).

Quantitatively transfer the $NaHSO_3$ to a 500-ml volumetric flask, add cooled, boiled deionized water to dissolve the salt and fill to the mark. This yields a 5 *mM* solution (5×10^{-3} *M*). Pipet 25 ml of this solution into a 50 ml volumetric flask and 25 ml into a 100 ml volumetric flask. Dilute each to the mark to yield solutions of 2.5 *mM* and 1.25 *mM* bisulfite, respectively. Pipet 5 ml of each of the three calibration solutions into 25 ml volumetric flasks. Using a pipet, add 5 ml of the NaH_2PO_4 buffer solution, 5 ml of the furfural solution, and 1 ml of sulfamic acid solution to each flask and also to an empty 25 ml volumetric flask (calibration standard with zero bisulfite content). Dilute to volume with water and mix well. With the instrument in the transmittance mode, adjust the zero and 100% T on the UV spectrophotometer with a solution of 5 ml of buffer and 1 ml sulfamic acid solution diluted to 25 ml with water (a blank) placed in both sample and reference cells. Change the instrument to the absorbance mode. Allow the calibration standards to stand at least 5 minutes but less than 20 minutes after preparation and then scan each of the four calibration solutions from 340*nM* to 260*nM* while retaining the blank solution in the reference cell.

Measure the absorbance (A) of the peak at 276 *nM* and calculate the reciprocal of absorbance (1/A). Plot 1/A (ordinate) *vs* the bisulfite concentration in millimoles per liter (abscissa) to yield a straight line function of the type y = a + b. Determine ordinate intercept (b) and the slope (a) of the function by a least squares calculation.

ANALYSIS OF SAMPLES

The samples must be free of particulate suspension and contact with the atmosphere should be minimized. The samples should have a bisulfite concentration of 1 - 5 *mM*. If upon analysis the level is too high, dilute the sample appropriately using quantitative techniques. If filtering or dilution is necessary, it should be done in an inert atmosphere dry bag or glove box. The samples should have an initial pH between 5 and 9.

Pipet 5 ml of the sample into a 25 ml volumetric flask. Add 5 ml of the NaH_2PO_4 buffer solution, 5 ml of the furfural solution, and 1 ml of the sulfamic acid solution. Add water to the mark and mix well. Analyze all the solutions using the method in the calibration section.

CALCULATIONS

Calculate the concentration of total sulfite plus bisulfite (S*IV*) in each solution according to the formula:

S*IV* concentration, *mM* = $5 \frac{B}{Y} (\frac{1}{A})$

where:

B = ordinate intercept of calibration straight line curve (A^{-1})

Y = slope of calibration straight line curve $(A^{-1} \frac{\text{m Moles}}{\text{l}}{}^{-1})$

APPENDIX F

DIRECTORY OF SEPARATOR MANUFACTURERS AND VENDORS

Ace Scientific Supply Co., Inc.
1420 E. Linden Ave.
Linden, N.J. 07036

Air Products & Chemical, Inc.
P. O. Box 538
Allentown, Pa. 18105

Allied Engineering & Production Corp.
2421 Blanding Ave.
Alameda, Calif. 94501

American Air Filter Co., Inc.
215 Central Ave.
Louisville, Ky. 40208

AMF Cuno Div.
American Machine & Foundry Co.
400 Research Parkway
Meriden, Conn. 06450

Amicon Corp.
Scientific Systems Div.
21 Hartwell Ave.
Lexington, Mass. 02173

Barnstead Co.
225 Rivermoor St.
Boston, Mass. 02132

Beaver Filter Corp.
P. O. Box 848
Port Ewen, N.Y. 12466

Belleville Wire Cloth Co. Inc.
135 Little St.
Belleville, N.J. 07109

The Bittner Corp.
181 Hudson St.
New York, N.Y. 10013

The Carborundum Co.
Graphite Product Div.
P. O. Box 577
Niagara Falls, N.Y. 14302

Chemical Equipment Corp.
7454 E. 46th St.
Tulsa, Okla. 74145

The Chemical Rubber Co.
18901 Cranwood Parkway
Cleveland, Ohio 44128

Clay Adams
Div. of Becton, Dickinson & Co.
299 Webro Rd.
Parsippany, N.J. 07054

Columbia Filter Co. Inc.
199 - 7th Ave.
Hawthorne, N.J. 07507

The DeLaval Separator Co.
350 Dutchess Turnpike
Poughkeepsie, N.Y. 12602

The Dow Chemical Co.
P. O. Box 1656
Indianapolis, Ind. 46206

The Duriron Co, Inc.
452 N. Findlay St.
Dayton, Ohio 45401

Eagle-Pitcher Industries, Inc.
American Bldg.
Cincinnati, Ohio 45202

Ertel Engineering Co.
62 Front St.
Kingston, N.Y. 12401

Filtros Plant-Ferro Corp.
601 W. Commercial St.
E. Rochester, N.Y. 14445

Fisher Scientific Co.
711 Forbes Ave.
Pittsburgh, Pa. 15219

General Nuclear Corp.
550 Fifth Ave.
New York, N.Y. 10036

Graham Manufacturing Co., Inc.
26 Harvester Ave.
Batavia, N.Y. 14020

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APPENDIX F (CONTINUED)

Heico, Inc.
Delaware Water Gap, Pa. 18327

F. R. Hormann & Co., Inc.
P. O. Box 229
Milldale, Conn. 06467

International Equipment Co.
300 Second Ave.
Needham Heights, Mass. 02194

International Sales Associates
116 N. Bellevue Ave.
Langhorne, Pa. 19047

Johns-Manville Products Corp.
22 E. 40th St.
New York, N.Y. 10016

Kern Chemical Corp.
854 S. Robertson Blvd.
Los Angeles, Calif. 90035

Komline-Sanderson Engineering Corp.
100 Holland Ave.
Peapack, N.J. 07977

Millipore Corp.
Ashby Rd.
Bedford, Mass. 01730

MSE, Inc.
811 Sharon Dr.
Westlake, Ohio 44145

Norton Co.
Plastics & Synthetics Div.
P. O. Box 350
Akron, Ohio 44309

Owens-Illinois, Inc.
Consumer & Tech. Products Div.
P. O. Box 1035
Toledo, Ohio 43601

Pall Trincor Corp.
459 Chestnut St.
Union, N.J. 07083

Pall Trinity Micro Corp.
Route 281
Cortland, N.Y. 13045

Pennwalt Corp.
3 Penn Center
Philadelphia, Pa. 19102

Perry Products Co.
1421 N. 6th St.
Philadelphia, Pa. 19122

Planchefs Lab Products
P. O. Box 1802
Ann Arbor, Mich. 48106

Pulverizing Machinery Div.
10 Chatham Rd.
Summit, N.J. 07901

Service Filter Corp.
7433 N. Harlem Ave.
Chicago, Ill. 60648

Straightline Filters, Inc.
Box 1911
Wilmington, Del. 19899

Technican Corp.
511 Benedict Ave.
Tarrytown, N.Y. 10591

Testing Machines, Inc.
400 Bayview Ave.
Amityville, N.Y. 11701

Tri-R Instruments, Inc.
48 Merrick Rd.
Rockville Center, N.Y. 11570

Vanton Pump & Equipment Corp.
201 Sweetland Ave.
Hillside, N.J. 07205

Zena Co.
723 - 22nd St.
Union City, N.J. 07087

APPENDIX G
PROCESS pH MONITORING SYSTEMS
BECKMAN

UNITS IN SYSTEM

Sensors

Glass Electrode	Standard glass pH electrode with short wide electrode bodies for strength and rapid replacement features - $32.00
Reference Electrode	Conventional reference with electrolyte reservoir or new Lazaran plastic unbreakable, chemically resistant electrode. Needs no electrolyte replenishment. - $32.00 - $125.00
Thermocompensator	Temperature sensitive resistance element for automatic correction of analyzer for temperature variation to read true pH - $47.00

Electrode Assembly

Flow Chamber	Available in stainless steel or polyvinyl dichloride useful at high pressure and over a wide range of temperature. Other materials are special order. Easy snam out electrode assembly - $150.00 - $210.00 Dimensions: Height - 14-1/4" (plus 6-5/16" for reservoir where necessary) Diameter - 3-1/4" Inlet - 1/2" NPT Outlet - 1/2" NPT Conduit - 1/2" NPT
Flow Chamber (Low pressure epoxy)	Useful for pH measurement in streams below 15 psig. Requires a unique 1" diameter reference electrode. 1/2" pipe fittings - $76.00

Submersion Chamber	Similar to standard flow chamber described above but designed for submersion in tank, etc. - $115.00 - $195.00
Separate Insertion Glands	Used for inserting electrodes separately into pipe, etc., threaded - $150.00 - $140.00

pH Analyzer

pH Indicator and Amplifier/Transmitter	May be purchased as separate units or as a single compact unit. Two models available. Differential amplification. Direct output from analyzers to grounded or ungrounded recorder or other readout device. Low drift and noise. Solid state circuitry. Scales for any 2, 5 or 10 pH units. Voltage or current output. Automatic or manual temperature compensation. Optional alarm contacts - $610.00

UNIVERSAL INTERLOCK, INC.

UNITS IN SYSTEM

Sensors

Glass Electrode	Standard glass pH electrodes with rugged construction manufactured by Micro Sensors, Inc. Combination electrode also available.
Reference Electrode	Available with either a hardwood plug liquid junction or a ceramic liquid junction. Sealed industrial reference available.
Thermocompensator	Automatic temperature compensator available.

Electrode Assembly

Flow Chamber	Available in PVC, Penton, and Teflon. Stainless steel special order. Can be purchased with built in preamplifier and features twist-open flow chamber for easy cleaning. $365.00 - $540.00 includes preamp, electrodes, temperature compensator and cell holder.

	Dimensions: Mounted on a 10" x 10" PVC plate Inlet - 1/2" NPT or 1" NPT Outlet - 1/2" NPT
Insertion Assembly	Unit contains electrodes, preamplifier, automatic temperature compensator and cell holders. Designed for pipe or tank installation - $470.00 - $595.00 Dimensions: Length - 10-1/8" Diameter - 3" Probe portion - 5" Housing with 2-1/2" NPT

pH Analyzer

Transmitter	All the signals preamplified at source. System terminates ground loop interference and is compatible with grounded or ungrounded instrumentation. Low drift and noise. Automatic or manual temperature compensation. Alarm contacts - $470.00 - $685.00

LEEDS AND NORTHRUP

UNITS IN SYSTEM

Sensors

Glass Electrode	Standard heavy duty type - $30.00
Reference Electrode	Low diffusion calomel reference requires less frequent filling. Non-fouling characteristics - $30.00
Thermocompensator	Available as part of system - $44.00

Electrode Assembly

Flow Chamber	Many available for various applications (flow, pressures, temperature, etc.). Non-fouling plastic (polypropylene) assembly eliminates clogging and electrode fouling in some applications. Available also in stainless steel - $109.00
Submersion Chamber	Many types available for various applications.

pH Analyzer

Amplifier	Preamplifier and amplifier are contained in one unit. Measurement of pH reading is performed by first generation system directly amplifying the differential mv signal - $608.00
Recorder	Hi-impedance unit capable of direct amplification and recording of mv electrode output - ~$1,000.00

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